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RESEARCH OF MICROSTRUCTURALLY DEVELOPED TOUGHENING
MECHANISMS IN CERAMICS. (U) ROCKWELL INTERNATIONAL
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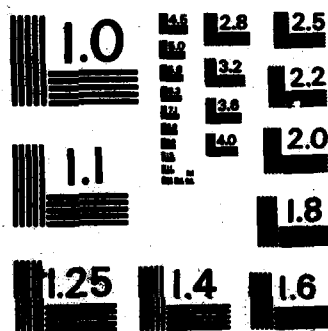
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RESEARCH OF MICROSTRUCTURALLY DEVELOPED TOUGHENING MECHANISMS IN CERAMICS

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- PART 1: DETERMINATION OF RESIDUAL SURFACE STRESSES DUE TO GRINDING IN POLYCRYSTALLINE Al_2O_3 (SC5117.13TR)
- PART 2: FACTORS INFLUENCING THE RESIDUAL SURFACE STRESSES DUE TO A STRESS-INDUCED PHASE TRANSFORMATION (SC5117.14TR)
- PART 3: COMPRESSIVE SURFACE STRENGTHENING OF BRITTLE MATERIALS (SC5117.15TR)
- PART 4: TRANSFORMATION TOUGHENING: THERMODYNAMIC APPROACH TO PHASE RETENTION AND TOUGHENING (SC5117.16TR)

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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) An x-ray diffraction technique has been used to measure the residual surface stresses induced by surface grinding in Al_2O_3 and in transformation- toughened Al_2O_3/ZrO_2 composites. For the Al_2O_3 , compressive stresses in the range 135 to 170 MPa were measured and were found to extend to a depth of 15 μm . It is believed that the compressive layer is produced by the elastic/plastic interaction of the abrasive grains with the ceramics. In the Al_2O_3/ZrO_2 composites, compressive surface stresses are a result of		

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→ the ZrO_2 phase transformation, which is induced by the stresses during grinding. Residual compressive surface stresses up to ≈ 1 GPa were measured. The role of the volume fraction of ZrO_2 , grain size and stabilizer oxide content in controlling the phase transformation are discussed, and their influence on the residual surface stress were measured. It was found that the volume fraction of ZrO_2 primarily controlled the magnitude of the compressive surface stress, but that other factors such as grain size influenced the depth of the compressive zone.

Finally, a fracture mechanics model is presented that allows the strengthening due to these residual stresses to be predicted. The model, which allows for crack closure effects, showed that the strengthening depends on the ratio of the compressive zone depth to surface crack length, and on the strength of the material in the absence of residual stresses.

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TECHNICAL REPORT NO. 13

**DETERMINATION OF RESIDUAL SURFACE STRESSES DUE TO GRINDING
IN POLYCRYSTALLINE Al_2O_3**

F.F. Lange, M.R. James and D.J. Green



DETERMINATION OF RESIDUAL SURFACE STRESSES DUE TO GRINDING
IN POLYCRYSTALLINE Al_2O_3

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ABSTRACT

Residual surface stresses introduced into polycrystalline Al_2O_3 during diamond grinding (320 grit) were examined with an x-ray diffraction technique commonly used for metals. Compressive stresses, estimated to be in the range of 135 MPa to 170 MPa and to extend $< 15 \mu m$ in depth, were observed at the surface. It is believed that the compressive surface layer coincides with the plastic layer produced by the elastic/plastic interaction of the abrasive grains with the ceramic. The results are discussed with regard to the effect of the compressive layer on the extension of surface cracks.

1. Introduction

Grinding, a common processing step for ceramics, introduces both plastic deformation and cracks into the material adjacent to the surface. The elastic/plastic interaction of abrasive grains with the ceramic surface has been considered analogous to a series of closely-spaced sliding, single-point indenters. As reviewed by Lawn and co-workers,^(1,2) a sharp indenter plastically deforms a small volume of material, which is proportional in size to the indenter impression. When the applied load is greater than a critical value, the sharp indenter also produces lateral (approximately parallel to the surface) and radial (normal to the surface) cracks. Intersecting lateral cracks are believed responsible for material removal during grinding; whereas the radial



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cracks will lead to strength degradation. Rice et al.⁽³⁾ have shown that two types of radial cracks exist within the groove produced by the plowing abrasive grains: 1) closely spaced cracks that traverse the groove produced by slip-stick and 2) longitudinal cracks which overlap one another along the length of the groove. The overlapping, longitudinal radial cracks produce the greatest strength degradation, resulting in a strength anisotropy when tensile strength is measured parallel and perpendicular to the grinding direction.

The residual surface stresses produced by the overlapping plastically-deformed volume elements associated with each grinding groove are of greatest concern in the present investigation. For the indentation produced by an isolated, sharp indenter, the material within the plastically deformed volume is in a state of compression and exerts tensile stresses on the radial crack fronts both at the surface and in the interior. These residual tensile stresses aid in crack extension when an external tensile load is applied to induce failure.⁽⁴⁾ However, when the plastically-deformed volume elements overlap one another, i.e., the suspected case for grinding, one would suspect that the complete surface would be plastically deformed and in a state of compression. If this were the case, the portions of the cracks within the compressive layer would be closed. These partially compressed cracks would be less effective in degrading strength than currently suspected from results of single-point indentation studies.⁽⁴⁾

The objective of this work was to determine if surface stresses are produced by surface grinding, and to estimate their magnitude and depth.

2. Approach

Surface residual stress measurements were made using an x-ray diffraction technique that is ideally suited for very shallow (~ few μm) depths and commercially employed by the metals industry. Authoritative reviews exist on this technique,^(5,6) which requires a polycrystalline sample so that a given set of (hkl) diffracting planes can be examined as a function of their angular rotation with respect to the specimen's surface. This is accomplished by



tilting the specimen and determining the Bragg angle for the chosen (hkl) planes as a function of the tilt angle. A change in the Bragg angle infers a surface strain. Conversion of the measured strain into surface stress is most easily accomplished by assuming isotropic elasticity. To partially compensate for anisotropic behavior along the particular (hkl) planes, the elastic constants specific to that plane are used rather than bulk values of the aggregate. Denoting these "x-ray elastic constants" as S_2 , isotropic elasticity theory yields $S_2 = (1 + \nu)/E$, where ν and E are Poisson's ratio and Young's modulus, respectively. The conversion also assumes that the surface is in a state of biaxial stress to the depth penetrated by the x-rays and that the principle strain axes are coplanar with the surface.

The x-ray elastic constants for the $\langle hkl \rangle$ direction can either be calculated with knowledge of the single crystal elastic compliance constants (see Nye⁽⁷⁾ or Dollé⁽⁸⁾) or determined by direct measurement. The experimental determination used here involved strain gauging a bar specimen (approximately $0.3 \times 0.6 \times 3$ cm) that had been annealed to help ensure minimal surface stresses. Surface strain determined with the strain gauge was first correlated to an applied surface stress by loading the bar specimen in 4-pt bending with an Instron Testing machine. The strain-gauged specimen was then placed in another 4-pt flexural loading jig mounted on the x-ray diffractometer to obtain correlation between the applied surface stress (as determined from the calibrated strain gauge) and the surface strain, as determined by the change in 2θ for the chosen (hkl), to obtain the elastic constants for the chosen $\langle hkl \rangle$ direction.

The particular computer-automated instrumentation and technique used here to determine surface stresses is similar to that described previously.⁽⁹⁾ Each measurement was carried out using eight tilt angles (0° to 45°). The peak of the diffraction profile at each tilt angle was determined by the apex of a least-squares parabola fit to the top portion of the profile. The profiles were very broad ($> 3^\circ$ 2θ full width, half maximum) and symmetric about the apex. To ensure that grinding did not introduce errors due to the principle strain components being inclined to the surface,⁽⁸⁾ some measurements were carried out



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at both positive and negative tilt angles and gave identical results. Typically, a single measurement of residual stress took three hours.

Hot-pressed Al_2O_3 (1500°C/2 hr), with an average grain size of 2 μm was chosen for the surface stress determinations.⁽¹⁰⁾ Initially, both Cu-radiation ($\lambda = 1.542\text{\AA}$) and Cr-radiation ($\lambda = 2.291\text{\AA}$) were used for the study, but preliminary work quickly showed the need for the shallower penetrating Cr-radiation.* The (602) diffraction peak was chosen for the Cu-radiation ($2\theta = 142^\circ$) and the (119) peak for the Cr-radiation ($2\theta = 135^\circ$). The x-ray elastic constants was determined for the respective $\langle hkl \rangle$ directions as described above. It was also calculated for the $\langle 119 \rangle$ direction using the Al_2O_3 single crystal compliance constants.⁽¹¹⁾ Based on the counting statistical accuracy⁽⁹⁾ of the (119) peak, the precision of the 2θ determination was calculated to be $\pm 0.030^\circ$. This corresponds to a statistical precision of ± 45 MPa when the (119) diffraction peak was used for surface stress determinations.

Three different bar specimens (approximately $0.3 \times 0.6 \times 1.0$ cm) were ground on four sides with a 320 grit diamond wheel removing ~ 25 μm of material with each pass.[†] Surface stresses in the direction of grinding were determined on one ground specimen with both Cu and Cr radiation. The second ground specimen was only examined with Cr radiation; subsequent determinations were made after 5 μm and then 10 μm of surface material was removed by polishing with 3 μm diamond paste. The third specimen was annealed at 1500°C/1 hr prior to surface stress examination. Surface stress determinations were repeated 2 or 3 times at different positions on the bar for each condition examined and the results averaged.

*Using the mass absorption coefficient for Al_2O_3 for either Cr or Cu radiation, and the possible path length for the given 2θ , 50% of the radiation is diffracted from an Al_2O_3 surface layer of 8 μm for Cr-radiation and 26 μm for Cu-radiation.

[†]Elgin, Inc., CD320R100BF-1/8-C4



3. Results

Table I lists the experimentally determined and calculated value of $E/(1 + \nu)$. The experimental value for the $\langle 119 \rangle$ direction was ~ 25% lower than the value calculated from the single crystal compliance constants.

Table II summarizes the surface stress results calculated with the experimentally determined value of $E/(1 + \nu)$. Values would be ~ 25% greater if single crystal results for $E/(1 + \nu)$ were used instead. Note that all surface stresses are compressive. Compressive stresses on the ground surface are substantial, viz ~ 135 MPa (to 170 MPa if single crystal results for $E/(1 + \nu)$ are used), whereas the 1 hr anneal reduced the stresses to within the limits

Table I
Values of $E/(1 + \nu)$

Radiation	Crystal Direction	$E/(1 + \nu)$ (GPa)	
		Experimental	Calculated
Cu	$\langle 602 \rangle$	212	--
Cr	$\langle 119 \rangle$	246	313

Table II
Surface Stress Determinations

Specimen	Radiation	Surface Treatment	Average Compressive Surface Stress* (MPa)
1	Cu	Ground	35 ± 16 (3)**
1	Cr	Ground	125 ± 7 (2)
2	Cr	Ground	145 ± 21 (2)
2	Cr	5 μ m Removed	70 ± 28 (2)
2	Cr	10 μ m Removed	83 ± 56 (2)
3	Cr	Annealed	29 ± 49 (3)

* Calculated using experimental value of $E/(1 + \nu)$.

** () Number of determinations.

of experimental error. Results of the deeper penetrating Cu-radiation (50% diffracted within a depth of 25 μ m from surface) and Cr-radiation (50% from a 8 μ m depth) and those obtained by polishing the surface to remove up to 10 μ m of material suggest that a majority of the compressive stresses are within a surface layer ≤ 15 μ m deep. Also note that most of the deviations are within that indicated from statistical counting errors (± 45 MPa) indicating that the stress state is uniform over the surface. The results of polishing suggest that even this procedure introduces a small amount of compressive residual stress.

4. Discussion

It has been shown that surface grinding with a commonly used diamond finishing wheel (150 grit) can produce substantial (135 to 170 MPa) compressive surface stresses that extend to a significant depth (≤ 15 μ m). It is reasonable to suspect that the compressive surface stresses arise due to the formation of a plastically-deformed surface layer produced by the elastic/plastic interaction of closely spaced grinding marks. This mechanism is suggested in the introduction. Thus, the plastically-deformed surface layer is in a state of compression.

It is expected that the surface compressive stresses will influence the catastrophic extension of surface cracks. The surface compressive stress will reduce the stress intensity factor of a surface crack subjected to an applied tensile stress. Given the large a/t ratio shown that the magnitude of this effect depends on the ratio of the crack length (a) to surface compressive layer depth (t).

Using the results for single point indentation studies, one can estimate a/t . Recent results of Anstis et al. (13) for the elastic/plastic interaction of the Vickers indenter, suggest the following relation:

$$a/t = c(a/d) = 0.09u (H^{1/4} E^{1/2} K_C^{-1} P^{1/4})^{2/3} \quad (1)$$

where d = indentation half-diagonal (radius of the grinding groove), H = material hardness, E = Young's Modulus, P = indenter load (grinding wheel's



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vertical load), K_C = critical stress intensity factor. For Al_2O_3 ,⁽¹⁰⁾ $H = 18$ GPa, $E = 400$ GPa, $K_C = 4.9$ MPa $m^{1/2}$,

$$a/t = 2 \alpha [P]^{1/6} , \quad (2)$$

where P is the vertical load of the diamond wheel in kilograms. Under normal grinding conditions $P < 1$ Kgm, thus $a/t \sim 2\alpha$. Examining the extreme cases when $t = d$ ($\alpha = 1$) and $t > a$ ($\alpha < 1/2$), i.e., the case where the crack is completely imbedded within the compressive layer, Green and Lange's⁽¹²⁾ analysis indicates that the strength increase due to the compressive layer for the cases where $\alpha = 1$ and $\alpha < 1/2$ are 30% and 100% of the compressive stress, respectively. For the Al_2O_3 used in the present work, the average flexural strength of ground specimens is 610 MPa.⁽¹⁰⁾ Data reported in Table II indicates a compressive stress of 135 to 170 MPa. Thus, if surface cracks were strength controlling and if the compressive stress could be removed (e.g., by annealing) without healing the surface cracks, one would expect that the average strength to decrease by a stress in the range of ~ 45 MPa ($\alpha = 1$, 30% of 135 MPa) to 170 MPa ($\alpha < 1/2$, 100% of 170 MPa).

The above discussion assumed that the closely spaced grinding grooves are uniform in depth and thus produced a plastic layer of uniform thickness. Surface topography measurements suggest that this is not the case for present day grinding wheels, viz, one or more grooves are much deeper than others. That is, the larger cracks associated with the deeper grooves will dominate strength determinations and the compressive surface layer may have less effect then indicated above.

In conclusion, it has been shown that significant surface compressive stresses result from surface grinding, i.e., the plastic interaction of the grinding wheel ameliorates the detrimental elastic interaction (surface cracks).

ACKNOWLEDGEMENT

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TECHNICAL REPORT NO. 14

**FACTORS INFLUENCING THE RESIDUAL SURFACE STRESSES
DUE TO A STRESS-INDUCED PHASE TRANSFORMATION**

D.J. Green, F.F. Lange and M.R. James



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FACTORS INFLUENCING THE RESIDUAL SURFACE STRESSES DUE TO A STRESS-INDUCED PHASE TRANSFORMATION

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1. Introduction

Residual surface compressive stresses are known to increase the strength of glasses and ceramics. Commercial glasses are strengthened by either tempering or ion-exchange methods. Kirchner et al.⁽¹⁻³⁾ have shown that the surfaces of different single phase ceramics can be placed in compression by a) diffusing ions which decrease the thermal expansion of the surface layer, b) glazing, and c) thermal quenching. Lange⁽⁴⁾ demonstrated that the surface of a two-phase (or multiphase) ceramic can be placed in compression when the minor phase increases its molar volume by a reaction which proceeds from the surface (e.g., oxidation, etc.). Molar volume changes can also be produced by structural transformations. Garvie et al.^(5,6) were the first to demonstrate that a compressive stress arises on the ground surfaces of polycrystalline cubic ZrO_2 materials containing precipitates of tetragonal ZrO_2 . The $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation, which involves a volume increase of ~3 to 5%, was induced by the grinding stresses. As demonstrated by Garvie and others, ceramics containing $ZrO_2(t)$ can be made stronger by surface grinding.*⁽⁵⁻¹¹⁾

The strengthening due to compressive surface stresses is a result of the residual stresses opposing the applied stresses. Green⁽¹²⁾ has shown that

*The $ZrO_2(t) \rightarrow ZrO_2(m)$ also increases fracture toughness, which also strengthens materials containing $ZrO_2(t)$.



the stress intensity factor of a surface crack subjected to both a residual compressive surface stress and an applied tensile stress depends on three factors: 1) the magnitude of the residual compressive stress, 2) the residual stress profile with respect to distance from the surface, and 3) the crack length (c) to compressive layer thickness (t) ratio (c/t). For a given residual stress, the stress intensity factor is minimized (and strength maximized) when the crack is fully embedded within a uniform compressive layer (c/t < 1).⁽¹²⁾ Thus, if one could engineer the magnitude, profile and depth of the compressive surface stress, one could minimize the effect of surface cracks on strength.

The goal of this investigation was to determine those factors that effect the magnitude, profile and depth of the compressive layer introduced by a structural phase transformation. As it will be described, the experimental portion of this work utilizes an x-ray diffraction technique to directly determine the state of residual stress.

2. Stress-Induced Structural Phase Transformations

If the surface of a large body undergoes a molar volume increase to a depth t, the biaxial compressive stress within this layer can be approximated by⁽¹³⁾

$$\sigma_c = \frac{1}{3} \left(\frac{\Delta V}{V} \right) \frac{E V_1}{(1-\nu)} \quad , \quad (1)$$

where $\Delta V/V$ is the molar volume increase, V_1 is the volume fraction of material with an increased molar volume, E is the elastic modulus, and ν , Poisson's ratio. When the compressive layer is small compared to the size of the body, tensile stresses, much smaller in magnitude relative to σ_c exist at depths greater than t.

The molar volume change of interest here is associated with a structural transformation induced by external stresses applied to the surface as, e.g., through the action of impinging, high velocity particles, or that of an abrasive grinding wheel. The depth to which material transforms will depend on both the magnitude of the applied stress as a function of the distance from the



surface, and the critical applied stress required to induce the transformation. This critical applied stress can be related to the thermodynamic parameters associated with the constrained transformation and the material's microstructure with the following analysis.

Let us assume that the volume element undergoing the stress-induced transformation is an individual grain or inclusion that is surrounded by a continuous matrix, which can be other grains of the same phase or another phase. The high temperature phase, constrained by the elastic matrix to low temperatures, will be labeled t , and its transformed structure will be labeled m , in reference to the ZrO_2 (tetragonal) \rightarrow ZrO_2 (monoclinic) transformation discussed in the experimental portion. Because the strain energy associated with the constrained transformation can be larger than the free energy gained by the structural transformation, the high temperature structure can be retained to much lower temperature than can be achieved in the unconstrained state. The retention of the high temperature phase also depends on size of the volume element undergoing the transformation. The size effect is due to the energetics of surface phenomena that accompany the transformation (viz. twinning and microcracking), and the fact that the free energy and strain energy terms scale differently with respect to the surface terms. The energetics of this transformation can be summarized with⁽¹⁴⁾

$$\Delta G_{t \rightarrow m} = -|\Delta G_c| + \Delta U_{se} f + \frac{6 \Sigma \gamma g}{D} \quad (2)$$

where $\Delta G_{t \rightarrow m}$ is the total change in free energy, $|\Delta G_c|$ is the magnitude of the free energy change associated with the unconstrained transformation (the negative sign preceding this term denotes that the transformation would be spontaneous in the unconstrained case), ΔU_{se} is the strain energy change, and $(1-f)$ is the reduction of strain energy due to accompanying surface phenomena that relieve either shear strains (twinning) or dilatational strains (microcracking). The term $6 \Sigma \gamma g / D$, is a summation of all the surface phenomena that accompany the transformation, viz., the interfacial energy change $(\gamma_m - \gamma_t g_s) A_m$, the energy of twin boundaries, $\gamma_T g_T A_m$, and the energy of microcracks, $\gamma_C g_C A_m$. In these terms, γ denotes energy per unit area associated with the particular surface, and g



denotes the area of the particular surface normalized by the interfacial area of the transformed inclusion, A_m (e.g., $g_s = A_t/A_m$, where A_t is the interfacial area of the high temperature phase). Since the units of Eq. (2) are energy/volume, the surface terms must be divided by the transformed volume ($\pi D^3/6$), hence the size of the transformed inclusion is present in the denominator of the surface term in Eq. (2). The surface term(s) dictate a size effect, i.e., a critical size exists below which the transformation is not spontaneous ($\Delta G_{t \rightarrow m} > 0$):

$$D_C = (|\Delta G_C| - \Delta U_{se} f) / (6 \Sigma \gamma g) \quad (3)$$

Let us now examine the case where a stress field must be applied to cause the transformation to be spontaneous. The types of stresses required are those that help reduce the constraint imposed by the elastic matrix. For example, if the transformation increases the volume of the inclusions hydrostatic tensile stresses would help relieve the matrix constraint. When the transformation occurs under an applied stress, the external loading system does work:(15)

$$W = \sigma_{ij}^a \epsilon_{ij}^t \quad (4)$$

where σ_{ij}^a are the components of the applied stress tensor, and ϵ_{ij}^t are the components of the transformational strain tensor. Since this work aids the transformation, it is a negative term as shown by

$$\Delta G_{t \rightarrow m} = -|\Delta G_C| + \Delta U_{se} f + \frac{6 \Sigma \gamma g}{D} - W \quad (5)$$

The minimum amount of work required to induce the transformation is obtained from $\Delta G_{t \rightarrow m} = 0$, or

$$W = -|\Delta G_C| + \Delta U_{se} f + \frac{6 \Sigma \gamma g}{D} \quad (6)$$

To reduce the complexity of Eq. (6) (for the general case, W contains 6 terms), let us assume that the transformation can be defined by one strain



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component, e.g., a simple isotropic volume increase where $\epsilon_{ij} = \epsilon_t = \Delta V/(3V)$, when $i = j$ and $\epsilon_{ij} = 0$ for $i \neq j$. For this case, the smallest applied hydrostatic tensile stress required to induce the transformation is given by

$$\sigma_a^C = (-|\Delta G_C| + \Delta U_{se}f + \frac{6\gamma\gamma_0}{D})/\epsilon_t \quad (7)$$

i.e., σ_a^C is the critical applied stress required to induce the transformation. Equation (7) shows that the conditions to cause the transformation to become spontaneous without an applied stress occurs when the summation in the numerator $\rightarrow 0$. Let us now examine the effects of each term in Eq. (7) holding all others constant. First, Eq. (7) shows that as $|\Delta G_C| \rightarrow 0$ (the case where the two unconstrained phases are in equilibrium), σ_a^C increases to approach $(\Delta U_{se}f + \frac{6\gamma\gamma_0}{D})/\epsilon_t$. Second, for the transformation involving a simple volume change, $\Delta U_{se} = k\epsilon_t^2/6$, (16) where k is the effective elastic modulus of the two phases given by

$$k = \frac{2E_m E_i}{(1 + \nu_m)E_i + 2(1 - 2\nu_i)E_m} \quad (8)$$

This relation shows that as the elastic modulus of the matrix (m) is increased, σ_a^C is increased. The third effect is concerned with the inclusion size (D). Its effect can better be illustrated by combining Eqs. (3) and (7) to obtain

$$\sigma_a^C = \frac{(-|\Delta G_C| + \Delta U_{se}f)(1 - \frac{D}{D_C})}{\epsilon_t} \quad (9)$$

Equation (9) shows that as $D \rightarrow 0$, $\sigma_a^C \rightarrow \infty$, and as $D \rightarrow D_C$, $\sigma_a^C \rightarrow 0$.

We are now able to examine the effect of $|\Delta G_C|$, ΔU_{se} and D on the transformation depth, (t), for a given type of surface stressing condition. Since the stress applied to the surface decreases with increasing depth, the stress at some depth $> t$ will be insufficient to satisfy the stress required to induce the transformation. The above arguments show that this depth can be maximized when the high temperature phase is just on the verge of transforma-



tion, i.e., where just a little stress is required to induce the transformation. This condition exists when $|\Delta G_c|$ is large, viz. $|\Delta G_c| \rightarrow \Delta U_{se} + 6\sigma_y g/D$, ΔU_{se} is small, viz. when the elastic modulus of the constraining matrix is low, and when $D \rightarrow D_c$. Conversely, the above arguments show that the depth of the transformed surface layer is minimized when $|\Delta G_c| \rightarrow 0$, ΔU_{se} is large (viz. large matrix modulus) and $D \rightarrow 0$.

3. Experimental

Surface stress measurements were carried out with a variety of two phase, Al_2O_3/ZrO_2 materials in which the ZrO_2 was retained in its tetragonal structure during cooling from the fabrication temperature. Surface stresses were introduced by surface grinding with a 320 grit diamond wheel to induce the $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation. The effect of changing the volume fraction of the $ZrO_2(t)$ (V_t), the chemical-free energy change ($|\Delta G_c|$) of the unconstrained $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation and the grain size of the $ZrO_2(t)$ (D) on the residual compressive stress were systematically investigated.

3.1 Surface Stress Determination

Surface residual stress measurements were made using an x-ray diffraction technique ideally suited for very shallow (microns) depths and commercially employed by the metals industry. Authoritative reviews exist on this technique.^(17,18) The technique requires a polycrystalline sample so that a given set of (hkl) diffracting planes can be examined as a function of their angular rotation with respect to the specimen's surface. This is accomplished by tilting the specimen and determining the Bragg angle for the chosen (hkl) planes as a function of the tilt angle. A change in the Bragg angle infers a surface strain. Conversion of the measured strain into surface stress is most easily accomplished by assuming isotropic elasticity. To partially compensate for anisotropic behavior along the particular (hkl) planes, the elastic constants specific to that plane are used rather than bulk values of the aggregate. Denoting these "x-ray elastic constants" as S_2 , isotropic elasticity



theory yields $S_2 = (1 + \nu)/E$, where ν and E are Poisson's ratio and Young's modulus, respectively. The conversion also assumes that the surface is in a state of constant biaxial stress to the depth penetrated by the x-rays, and that the principle strain axes are coplanar with the surface.

The x-ray elastic constants for the (hkl) direction can either be calculated with knowledge of the single crystal elastic compliance constants (see Nye⁽¹⁹⁾ or Dolle⁽²⁰⁾) or determined by direct measurement. The experimental determination used here involved strain-gauging a bar specimen (approximately 0.3 x 0.6 x 3 cm) that had been annealed to help ensure minimal surface stresses. Surface strain determined with the strain gauge was first correlated to an applied surface stress by loading the bar specimen in 4-pt bending with an Instron testing machine. The strain-gauged specimen was then placed in another 4-pt flexural loading jig mounted on the x-ray diffractometer to obtain correlation between the applied surface stress (as determined from the calibrated strain gauge), and the surface strain as determined by the change in 2θ for the chosen (hkl) to obtain the elastic constants for the chosen (hkl) direction.

The particular computer-automated instrumentation and technique used here to determine surface stresses is similar to that described previously.⁽²¹⁾ Each measurement was carried out using eight tilt angles (0° to 45°). The peak of the diffraction profile at each tilt angle was determined by the apex of a least-squares parabola fit to the top portion of the profile. The profiles were very broad ($>3^\circ$ 2θ full width half maximum) and symmetric about the apex. To ensure that grinding did not introduce errors due to the principle strain components being inclined to the surface,⁽²⁰⁾ some measurements were carried out at both positive and negative tilt angles and gave identical results. Typically, a single measurement of residual stress took three hours.

For the present work, both $\text{CuK}\alpha$ ($\lambda = 1.542\text{\AA}$) and $\text{CrK}\alpha$ ($\lambda = 2.291\text{\AA}$), radiations were used in this study. The Al_2O_3 (602) diffraction peak was chosen for the Cu radiation ($2\theta = 142^\circ$), and the (119) peak chosen for the Cr radiation ($2\theta = 135^\circ$). Table 1 lists the penetration depths (normal to surface) for both $\text{CuK}\alpha$ and $\text{CrK}\alpha$ at $2\theta = 142^\circ$ and 135° , respectively, calculated for the mass absorption coefficients and densities of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites for the



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Table 1
Depth (m) of Diffracted X-rays vs ZrO_2

Radiation	Volume % ZrO_2 *							% Diffracted
	7.5	15	20	30	40	52	60	
CuK α				12.8				50
($2\theta = 142^\circ$)				114.0				95
CrK α	6.5	5.5	4.9	4.1	3.5	3.0	2.6	50
($2\theta = 135^\circ$)	28.1	23.6	21.2	17.6	15	12.9	11.3	95

*Alloy additions to ZrO_2 (viz Y_2O_3 or CeO_2) not taken into account in calculations.

different composites investigated with each radiation. This table illustrates that CuK α is much more penetrating than CrK α , and the penetration depth decreases with increasing vol % ZrO_2 .

It should be noted that the surface stress determination is a mean value of stresses integrated over the depth penetrated by the radiation used (weighed by an exponential function due to absorption). If the residual surface stress is not constant with increasing depth and/or its depth is less than the depth penetrated by diffraction x-rays, one would expect different mean values for different characteristic x-rays.

Table 2 lists the values of $E/(1 + \nu)$ for the two sets of planes obtained by the experimental method described above, and through calculations using single crystal compliance constants.⁽²²⁾ Note that the calculated value of $E/(1+\nu)$ is ~ 25 % greater.

Table 2
Values of $E/(1 + \nu)$

Radiation	Crystal Direction	$E/(1 + \nu)$ (GPa)	
		Experimental	Calculated
Cu	$\langle 602 \rangle$	212	--
Cr	$\langle 119 \rangle$	246	313



3.2 Materials

One series of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites containing 30 volume percent (v/o) ZrO_2 were investigated in which the ZrO_2 contained between 9 and 22 mole percent (m/o) CeO_2 . The unconstrained $t \rightarrow m$ transformation temperature decreases with increasing m/o CeO_2 .⁽²³⁾ Thus, increasing CeO_2 additions decreases the room temperature value of $|\Delta G_c|$. The fabrication and sintering (1600°C/2 hr) of these materials are reported elsewhere.⁽²³⁾

A second $\text{Al}_2\text{O}_3/\text{ZrO}_2$ series was fabricated to contain different v/o ZrO_2 . For this series, Y_2O_3 was used as the alloy addition, which was incorporated by the manufacturer.* The Y_2O_3 content was increased with increasing v/o ZrO_2 in the composite, viz. 1.37 m/o Y_2O_3 for composites containing 7.5 and 15 v/o ZrO_2 , 2.50 m/o Y_2O_3 for the 30, 40 and 50 v/o ZrO_2 composites, and 3.65 m/o Y_2O_3 for the 60 v/o ZrO_2 composite.[§] Since the elastic modulus of the composites decreases with increasing ZrO_2 v/o, the m/o Y_2O_3 must be increased to retain the tetragonal structure, as discussed elsewhere.⁽¹⁴⁾ A colloidal/filtration route was used to consolidate milled composite powders in this series similar to that described elsewhere.⁽²⁴⁾ Sintering was carried out at 1600°C/2 hr.

Three other $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites containing 7.5 v/o ZrO_2 (no Y_2O_3), 6.6 v/o ZrO_2 (2.0 m/o Y_2O_3), and 30 v/o ZrO_2 (2.0 m/o Y_2O_3) were also investigated. These materials were hot-pressed (1500°C/ 2 hr) as described elsewhere.⁽²⁵⁾

3.3 Experiments

All surface grinding was carried out with a 320 grit diamond wheel[†] using a Dual Surface grinding machine. Approximately 10 μm of material was removed during each pass. Bar specimens (approximately 0.3 x 0.6 x 1.0 cm) were

*Zircar Products Inc., Florida, N.Y.

§ Y_2O_3 content determined by Spectrochemical Laboratories Inc., Pittsburgh, PA.

†Elgin, Inc., CD320-R100-BF-1/8-C4



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used. The crystal structure of the ZrO_2 adjacent to the surface was determined by x-ray diffraction analysis. The approximate monoclinic/tetragonal ratio was determined with the $(\bar{1}\bar{1}1)$ monoclinic/ (111) tetragonal peak height ratio.

The first experiments, carried out with the hot-pressed materials, did not involve surface stress measurements. These experiments simply involved careful polishing ($3\text{ }\mu\text{m}$ diamond paste) of the ground surface, and determining the monoclinic/tetragonal ratio as a function in the depth of material removed. $CuK\alpha$ radiation was used for these measurements.

Surface stress measurements were carried out on the Al_2O_3/ZrO_2 (30 v/o) composite series containing the different CeO_2 alloy additions. All specimens were ground during the same period. Both $CuK\alpha$ and $CrK\alpha$ radiation was used for surface stress determinations. Surface stress determinations were redetermined for several specimens with $CrK\alpha$ radiation after annealing at $1650^\circ\text{C}/2\text{ hr}$.

To determine the effect of grain size on surface stresses, the sintered $Al_2O_3/30\text{ v/o } ZrO_2$ (2.50 w/o Y_2O_3) material was cut into a number of bar specimens, each of which were heat treated for 2, 8, 16 and 24 hrs at 1650°C to increase the as-fabricated ZrO_2 grain size. Grain size distributions were determined on SEM micrographs using a Quantimet Image Analyzer. Approximately 600 grains were examined for each heat treatment. All but one of these specimens were then ground during the same period for surface stress determinations. Two specimens (annealed 0 hr and 24 hr, then ground) were carefully polished to remove, in subsequent steps, between 2 to $4\text{ }\mu\text{m}$ of surface material. Surface stresses were redetermined after each polishing step in an attempt to determine the depth of the surface stress layer and the stress profile.

Surface stress determinations were carried out for the series surface-ground, sintered composites containing increasing v/o of ZrO_2 .



4. Results

4.1 Surface Phase Analysis

Table 3 lists the monoclinic/tetragonal phase ratio for as-sintered (or as-annealed) and as-ground surfaces. For the series containing the CeO_2 alloying addition to ZrO_2 (Table 3a), note that the ZrO_2 in the sintered materials alloyed with both 9 and 10 m/o CeO_2 was not fully tetragonal. Also for the same series, the monoclinic content of ground surfaces with either $\text{CuK}\alpha$ or $\text{CrK}\alpha$ decreased with increasing m/o CeO_2 .

Table 3a
Monoclinic/Tetragonal Phase Ratio for $\text{Al}_2\text{O}_3/30$ v/o ZrO_2
Series Alloyed with CeO_2

CeO ₂ Content	Ratio of Peak Intensities (111) _m /(111) _t		
	Sintered Surface	Ground Surface	
	CuK α *	CuK α *	CrK α
9	0.33	0.97	1.07
10	0.29	0.60	0.82
13	<0.02	0.17	0.15
14	<0.02	0.085	0.11
15	<0.02	0.064	0.070
17	<0.02	0.035	0.045
18	<0.02	0.027	<0.02
20	<0.02	<0.02	<0.02
22	<0.02	<0.02	<0.02

* ± 0.02 .

For the second series listed in Table 3b, the materials most sensitive to transformation, both during fabrication and subsequent surface grinding, were those in which the ZrO_2 was alloyed with only 1.37 m/o Y_2O_3 . A 20 v/o ZrO_2 composite was also fabricated with the same ZrO_2 (+1.37 m/o Y_2O_3) powder, but it



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contained approximately equal proportions of monoclinic and tetragonal ZrO_2 and was deemed unsuitable for consistent experimentation. Note that surface grinding generally increased the monoclinic content of the surface.

Figure 1 illustrates the m/t intensity ratio for the three hot-pressed materials which were sequentially polished to remove surface material and re-examined for phase content. Note the difference in the monoclinic depth for the 7.5 v/o ZrO_2 (0 m/o Y_2O_3) and 6.6 v/o ZrO_2 (+2 m/o Y_2O_3). The depth of the transformed layer for the material alloyed with Y_2O_3 is much shallower relative to that containing no Y_2O_3 . Also note that the 30 v/o ZrO_2 composite had a transformed layer intermediate in depth to the other two.

Table 3b
Monoclinic/Tetragonal Phase Ratio

v/o ZrO_2	m/o Y_2O_3	Sinter (Anneal) Condition	Ratio of Peak Intensity (111)m/(111)t		
			Sintered Surface CuK α *	Ground Surface CuK α *	CrK α
7.5	1.37	1600°C/2 hr	0.02	0.22	0.14
15	1.37	1600°C/2 hr	0.09	0.38	1.01
30	2.5	1600°C/2 hr	<0.02	0.06	0.21
30	2.5	(1650°C/2 hr)	<0.02	0.09	**
30	2.5	(1650°C/8 hr)	<0.02	0.09	**
30	2.5	(1650°C/16 hr)	0.03	0.08	**
30	2.5	(1650°C/24 hr)	<0.02	0.10	**
40	2.5	1600°C/2 hr	<0.02	<0.02	<0.02
50	2.5	1600°C/2 hr	<0.02	0.07	**
60	3.65	1600°C/2 hr	<0.02	0.05	0.12

* ± 0.02 .

** - data not recorded.

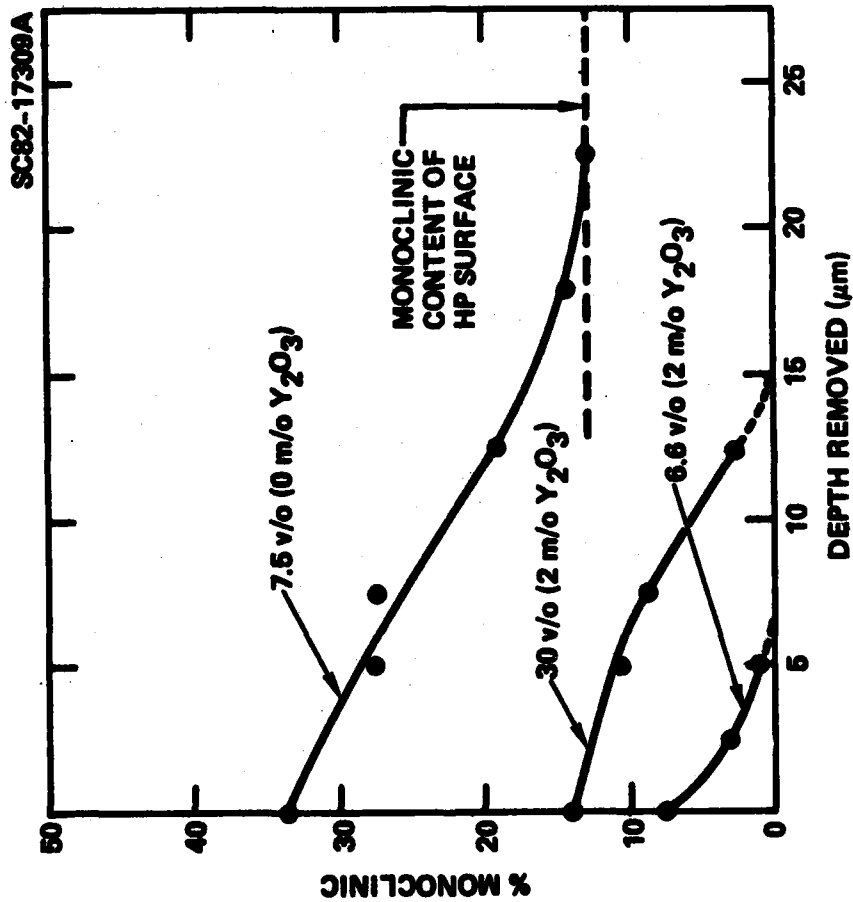


Fig. 1 Monoclinic ZrO_2 content as a function of depth removed by polishing, for various Al_2O_3/ZrO_2 composites.



4.2 Surface Stress of Series Alloyed with CeO₂

Figure 2 shows that the average compressive stress, determined with the shallower penetrating CrK α radiation, decreases slightly with increasing CeO₂ alloy addition to ZrO₂. Ground and annealed surfaces are nearly stress-free. Table 4 reports the surface stress for the same ground materials, as determined with the deeper penetrating CuK α radiation (9 and 10 m/o CeO₂ materials were not used). The surface compressive stresses at lower CeO₂ are smaller relative to CrK α determinations and appear to reverse to tension at higher CeO₂ contents; the single determinations made with CuK α radiation lie within the statistical counting errors (± 23 MPa) and may negate this conclusion.

4.3 Effect of ZrO₂ Grain Size

The average ZrO₂ grain size for the Al₂O₃/30 v/o ZrO₂ (+2.5 m/o Y₂O₃) materials sintered at 1600°C/2 hr and heat-treated at 1650°C for 2, 8, 16 and 24 hrs are 1.3 μ m, 1.4 μ m, 1.8 μ m, 2.2 μ m and 3.4 μ m, respectively. Figure 3 illustrates typical micrographs of the extreme conditions. Figure 4 illustrates the small increase for the average surface compressive stress (CrK α radiation) with increasing grain size.

Figure 5a and 5b illustrate the results of the stress profile experiments carried out on the Al₂O₃/30 v/o ZrO₂ (+2.5 m/o Y₂O₃) composite (CrK α radiation). A polynomial correction was applied to the raw data to compensate for the stress relaxation that occurs when a portion of the surface is removed.⁽²⁶⁾ These figures show that the compressive stress decreases with increasing distance from the initial ground surface. A residual compressive stress of ~ 100 MPa still persisted after a large portion of the initial surface was removed, suggesting that the polishing operation may produce some transformation and/or plastic deformation that results in a surface compressive stress.

A comparison of the two sets of data (Fig. 5a and b) show that the larger grain size material (annealed 1650°C/24 hr, ground) produces a slightly deeper compressive stress layer (~ 18 μ m) relative to smaller-grained material (as-sintered, ground) for which the depth was estimated to be ~ 13 μ m. Also note

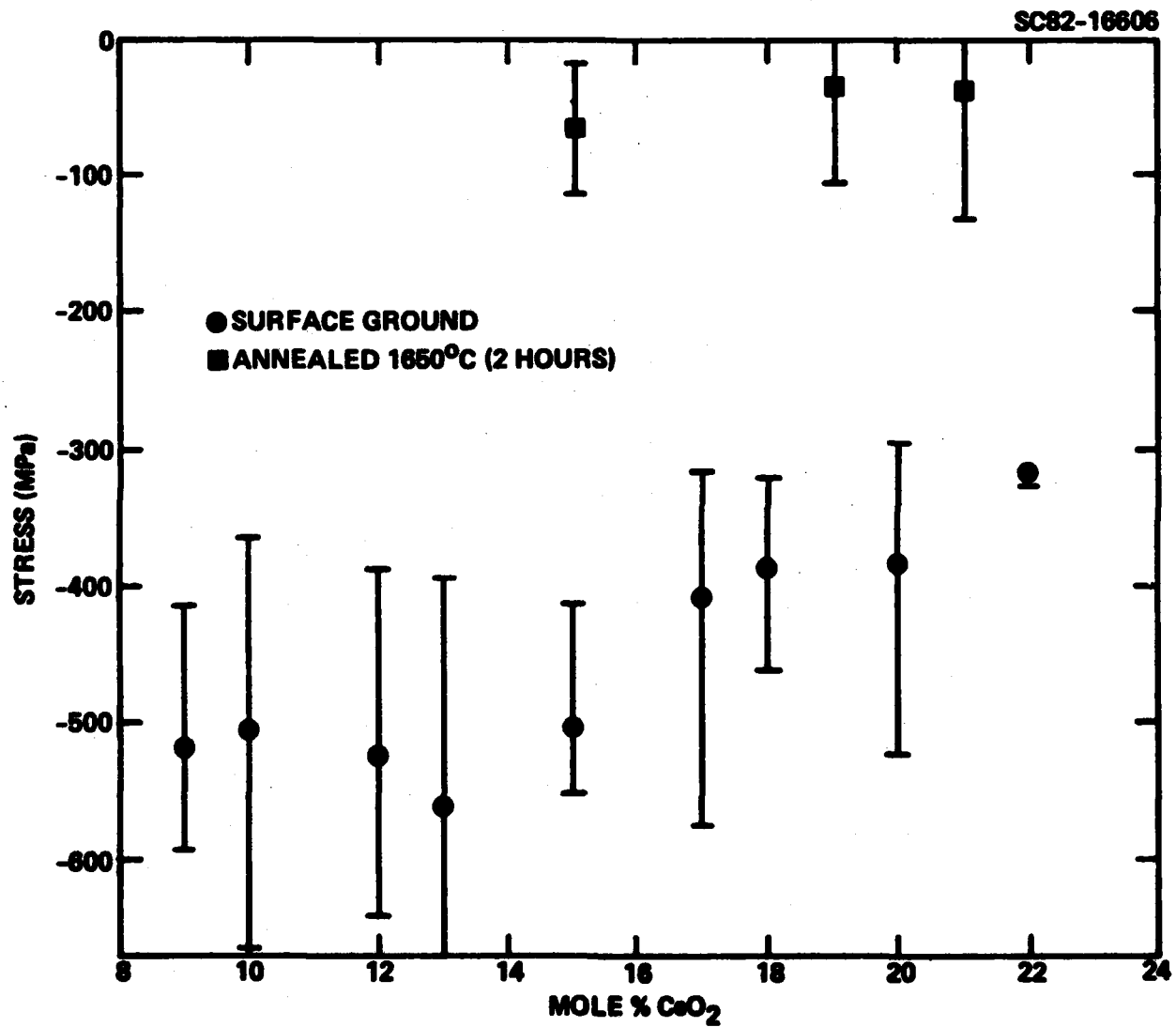


Fig. 2 Surface residual stress measurements for Al₂O₃/30 vol% ZrO₂ composites, in which ZrO₂ is alloyed with various amounts of CeO₂. The errors bars represent range of experimental results.



Table 4
Surface Residual Stresses (CuK α Radiation)

Mole % CeO ₂	Surface Stress* (MPa)
12	-30
13	-21
14	+17
15	+ 0
17	- 1
18	+ 2
19	+18
20	+15
21	+21
22	+19
Estimated Error \pm 23 MPa	

*Compressive stress is negative.



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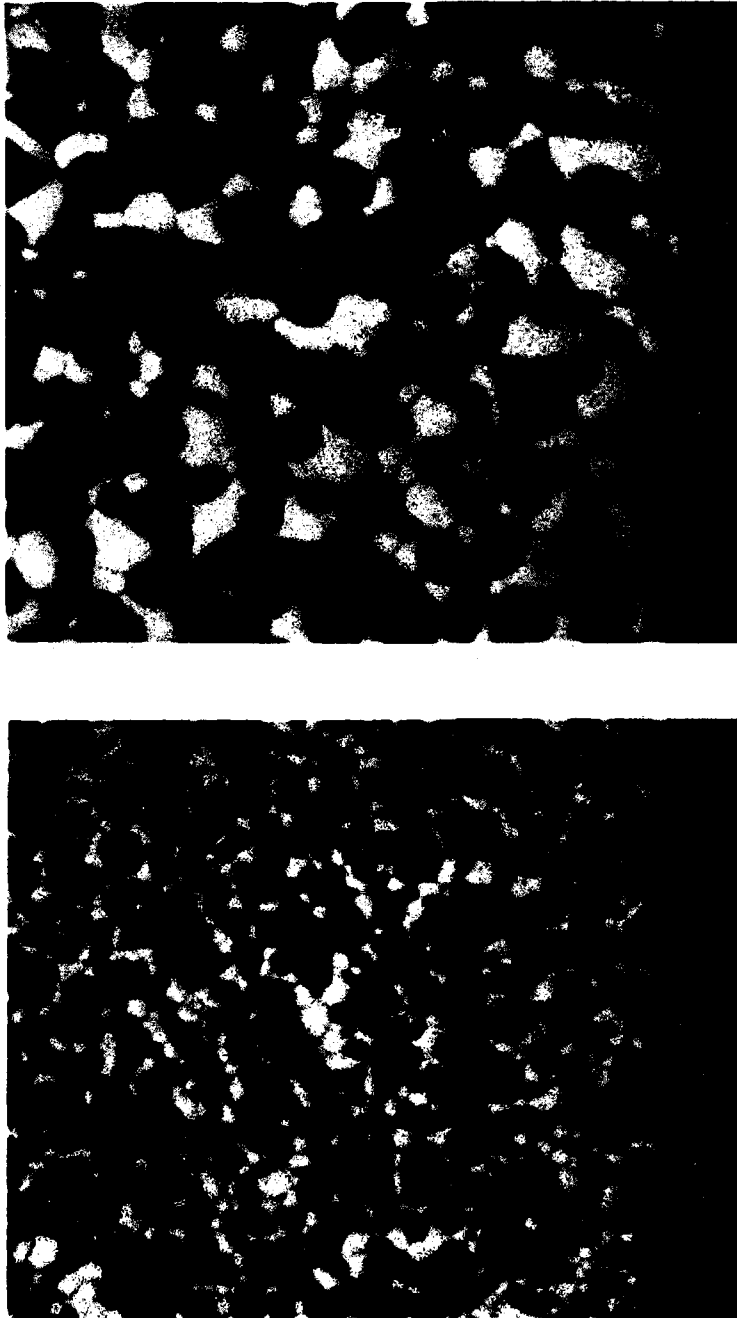


Fig. 3 Comparison of microstructures of $\text{Al}_2\text{O}_3/30$ vol% ZrO_2 composites heat treated; a) 1650°C (2 hours) b) 1650°C (24 hours). Micrograph obtained using backscattered electron mode in SEM.

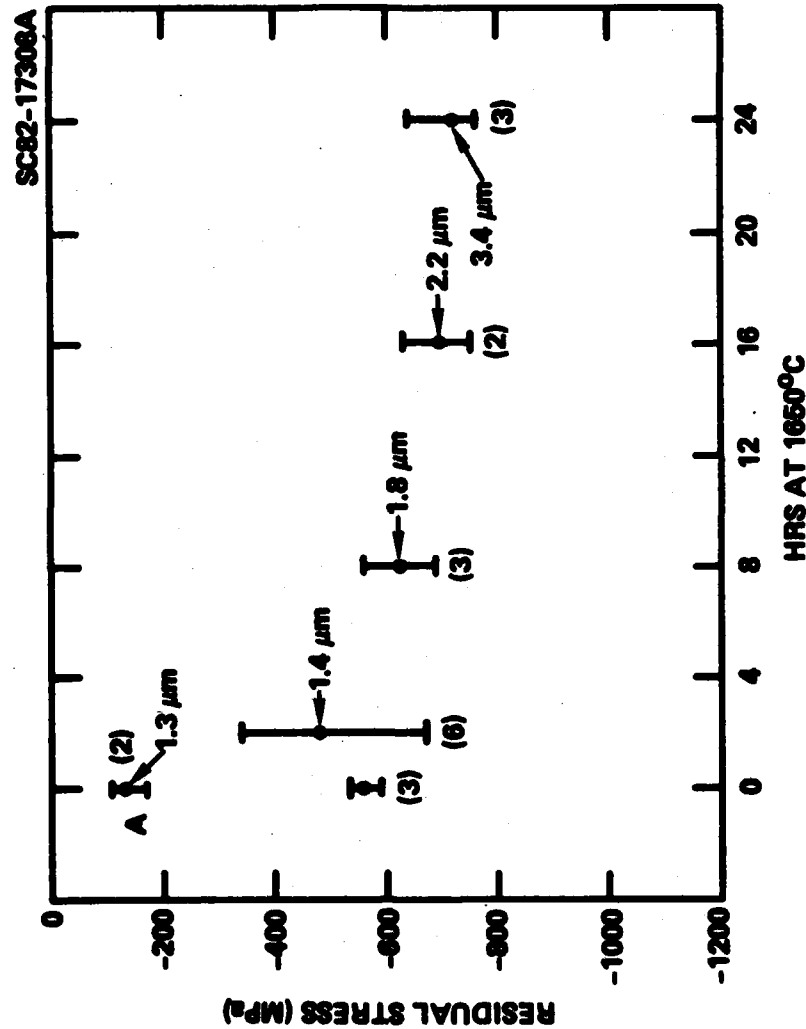


Fig. 4 Surface residual stress measurements for a series of surface-ground Al₂₀3/30 vol% ZrO₂ specimens heat treated at 1650°C for various times. Included is average ZrO₂ grain size and stress determinations on an annealed specimen (A).

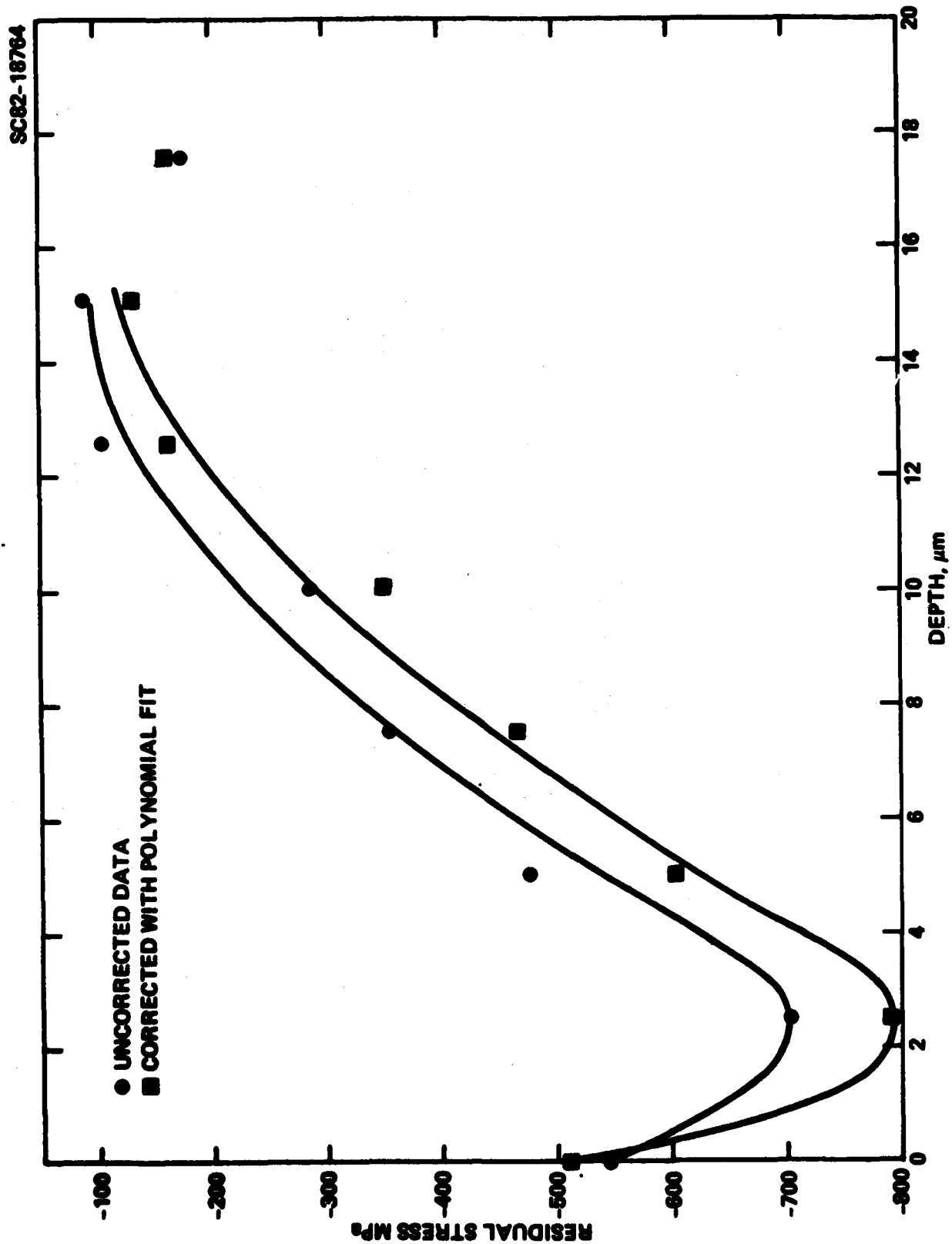


Fig. 5a Experimentally-determined and corrected residual stress profiles for an Al 203/30 vol% ZrO₂ specimen (Av. ZrO₂ grain size, 1.3 μm).



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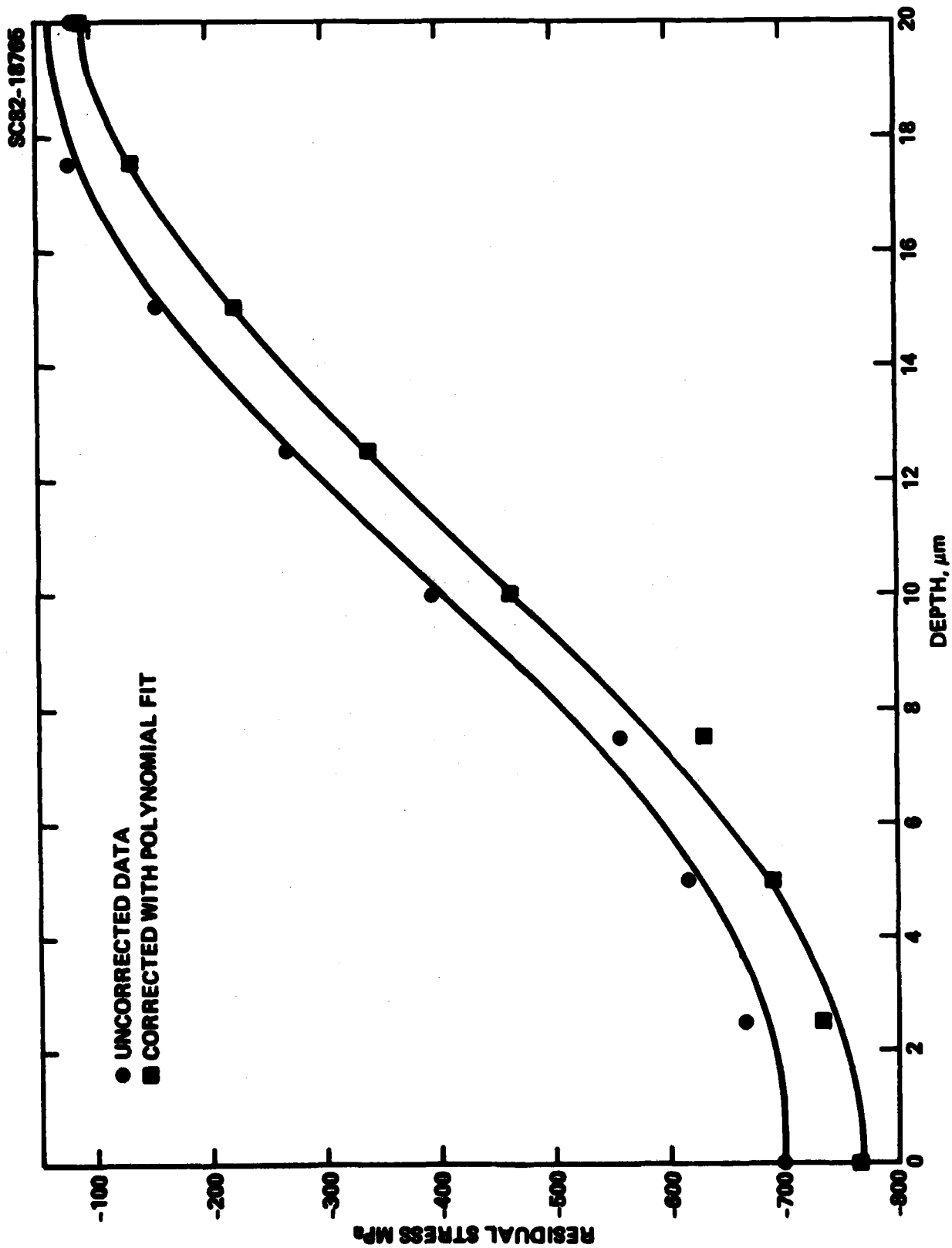


Fig. 5b Experimentally-determined and corrected residual stress profiles for an Al₂₀₃/30 vol% ZrO₂ specimen (Av. ZrO₂ grain size, 3.4 μm).



that the depth of the transformed layer for hot-pressed Al_2O_3 30 v/o ZrO_2 (+2 m/o Y_2O_3) as estimated by successive polishing and XRD measurements (Fig. 1) is nearly identical to compressive larger depths shown in Fig. 5a, which was determined for a nearly identical material (composition and microstructure).

4.4 Effect of ZrO_2 Volume Fraction

Figure 6 illustrates that the residual compressive stresses ($\text{CrK}\alpha$ radiation) increases with increasing v/o ZrO_2 retained in the sintered material in its tetragonal structure. Namely, the compressive stress can exceed 1 GPa. It should be noted that these results may be somewhat modified by the fact that ZrO_2 is a strong absorber of x-rays (see Table 1). That is, the depth sampled with the $\text{CrK}\alpha$ radiation for 7.5 v/o ZrO_2 is about three times that for the 60 v/o ZrO_2 , which may bias the apparent stress magnitude to higher values with increasing ZrO_2 content.

5. Discussion

All evidence suggests that the residual compressive surface stresses introduced by grinding $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{t})$ composites are produced by the molar volume change associated with the $\text{ZrO}_2(\text{t}) \rightarrow \text{ZrO}_2(\text{m})$ transformation. In all materials examined, the stresses applied to the surface by the abrasive grinding media were sufficient to induce this transformation as indicative of both XRD phase examination and surface stress determinations. As indicated by comparative results for $\text{CuK}\alpha$ and $\text{CrK}\alpha$ radiation, the magnitude of the residual surface stress was dependent on the penetration depth of the diffracting x-rays. As suggested by Eq. (1), the magnitude of these residual compressive surface stresses are primarily controlled by the volume fraction of tetragonal ZrO_2 (Fig. 6).

Although the magnitude of the residual surface stress is primarily controlled by the $\text{ZrO}_2(\text{t})$ volume fraction, data indicates that the depth of the transformed material and the residual stress profile depends on $|\Delta G_c|$ and grain size, D , which determine the critical applied stress required to induce the transformation. As discussed in Section 2, the transformed depth should increase with increasing $|\Delta G_c|$ and/or ZrO_2 grain size (D).



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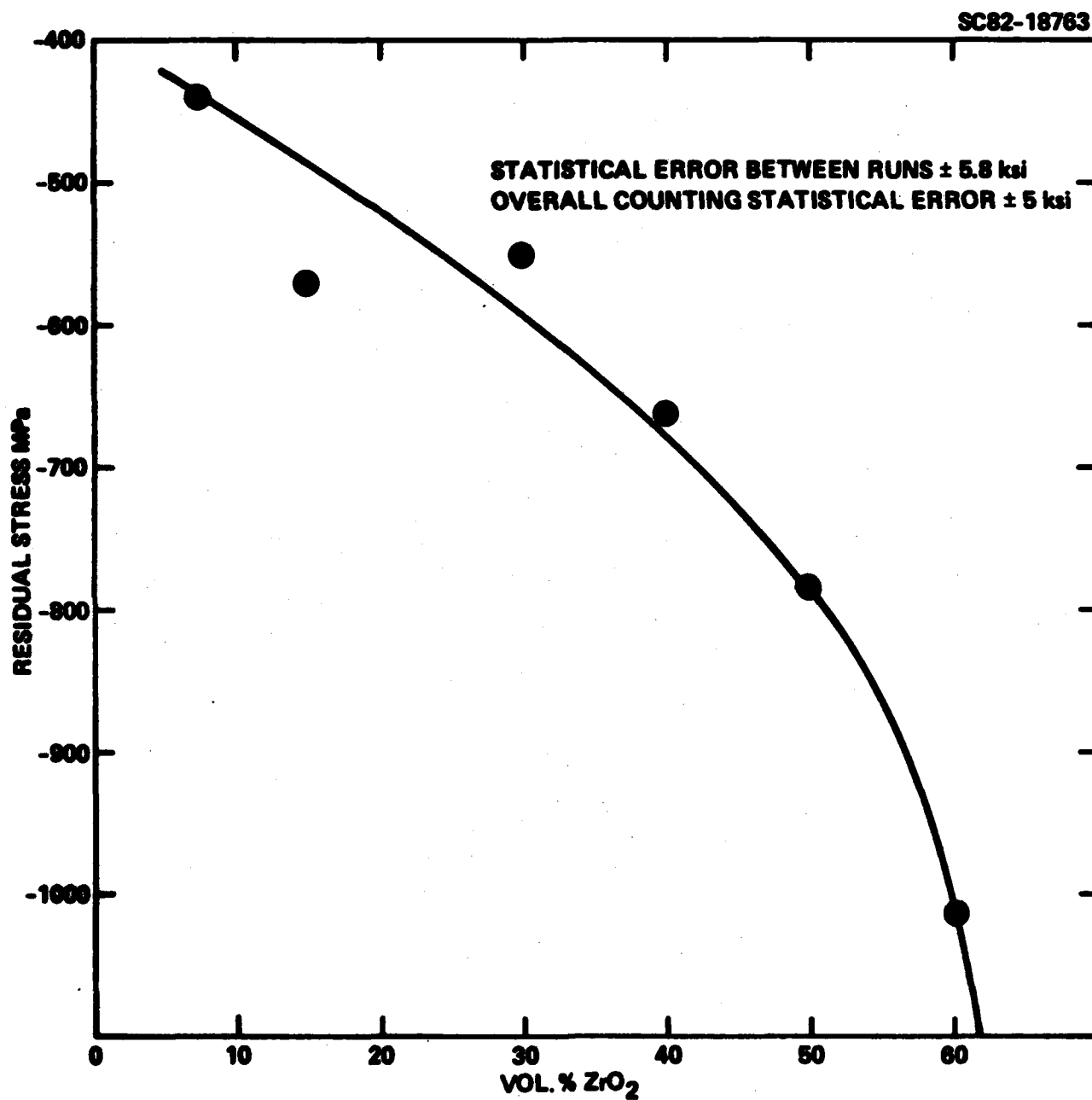


Fig. 6 Average residual surface stress measurements for a series of Al_2O_3/ZrO_2 composites.



Both Y_2O_3 and CeO_2 decrease $|\Delta G_c|$ at room temperature. Figure 1 shows that for nearly equivalent ZrO_2 contents (6.6 v/o vs 7.5 v/o), the depth of the transformation layer was much shallower for the case where the ZrO_2 was alloyed with the Y_2O_3 . When CeO_2 was alloyed with the ZrO_2 , residual compressive stresses were only observed with the $CuK\alpha$ radiation for materials with the least CeO_2 content, whereas the residual stress exhibited only a slight decrease with increasing CeO_2 content when determined with the shallower penetrating $CrK\alpha$ radiation.

Equation (8) also suggests that the depth of the transformed layer should also increase as $D \rightarrow D_c$. Data presented in Fig. 7 is consistent with this hypothesis, i.e., the transformation depth for the material examined increased from $\sim 13 \mu m$ to $\sim 18 \mu m$ for a grain size increase of $1.3 \mu m$ to $3.4 \mu m$.

Further stress profiling experiments are now underway to better substantiate the dependence of the transformation depth on $|\Delta G_c|$ and grain size, D .

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TECHNICAL REPORT NO. 15

**COMPRESSIVE SURFACE STRENGTHENING
OF BRITTLE MATERIALS**

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**COMPRESSIVE SURFACE STRENGTHENING
OF BRITTLE MATERIALS**

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ABSTRACT

A theoretical approach has been put forward for predicting the strengthening of materials by the introduction of surface compressive stresses. An approximate technique was used to determine the closure length of a surface crack which extend through the compressive surface layer. The stress intensity factor of the partially closed crack was then determined for the case of an applied tensile stress with the assumption that the residual surface compressive stress was uniform within the surface layer. The analysis shows that the strengthening depends on the magnitude and depth of the compressive surface stress and the strength of the body in the absence of the residual stress.



I. INTRODUCTION

The strength of ceramics or glasses can often be increased by placing their surfaces into compression. These techniques include ion exchange, tempering, glazing, surface chemical reactions and stress-induced phase transformations. Although most of these techniques are well-recognized, a theoretical approach to optimization of the strengthening has not been developed. The aim of this paper is to use fracture mechanics to predict the amount of strengthening obtained for a particular residual stress distribution and in particular, to identify the important material and process parameters that need to be controlled. Such an approach would be expected to be relatively straightforward as many crack loading geometries have been solved. The presence of residual stresses does, however, lead to complications in the analysis, when the crack is only partially open at the failure condition and these difficulties have impeded the theoretical developments. Partial crack closure in simple configurations have been analyzed by several authors,⁽¹⁻⁵⁾ while for more complex situations numerical approaches have been used.⁽⁶⁻¹⁰⁾ In this paper a simplified approach to the crack closure problem for surface cracks is used and the stress intensity factor is then derived in a more rigorous fashion. The amount of strengthening is then determined by inserting the appropriate fracture criterion, thus identifying the important parameters.



II. THEORETICAL APPROACH

Consider an infinitely-long isotropic plate, width W , which is subjected to the residual stress distribution shown in Fig. 1. This problem is a limiting case of an analysis by Oel and Frechette,⁽¹¹⁾ and it can be shown that the surface (σ_c) and interior (σ_t) stress are given by

$$\sigma_c = \frac{-E \epsilon}{(1 - \nu)} \left(\frac{W - 2t}{W} \right) \text{ for } t > X > (W - t) \quad (1)$$

and

$$\sigma_t = \frac{2E \epsilon t}{(1 - \nu)W} \text{ for } t < X < (W - t) \quad (2)$$

where E is the Young's modulus, ν the Poisson's ratio and ϵ is the linear strain associated with the uniform volume change that occurs at the surface. As can be determined from Eqs. (1) and (2), a volume increase at the surface leads to a surface compressive stress and a compensating interior tensile stress. Such a residual stress distribution is expected to be a reasonable approximation for many glazing, enamelling or sealing operations. For the situations where the surface layers are a different material than the inside Eqs. (1) and (2) become slightly more complicated.⁽¹¹⁾

The production of ceramic bodies with a compressive surface layer is expected to lead to strengthening, as the compressive stress will oppose applied tensile stresses, particularly when fracture occurs from flaws at or near the surface. When the flaw is completely subjected to the compressive stress the increase in strength of the body ($\Delta\sigma_f$) will be simply given by

$$\Delta\sigma_f = - \sigma_c \quad (3)$$

In many cases, however, it is expected that the flaw size will be greater than the depth of the compressive zone and it is important to be able to predict the amount of strengthening that will occur. As can be seen from Eq. (1) this will



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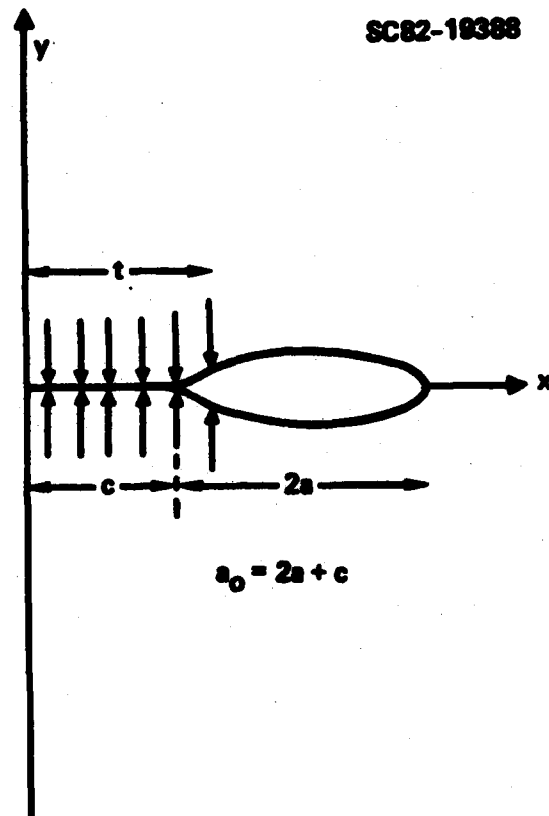


Fig. 1 Residual stress distribution in isotropic flat plate, in which surface has undergone a uniform volume increase.



lead to an optimization process, as the more shallow the depth of the compressive zone, the larger is the surface compressive stress.

Consider now a semi-infinite body containing a surface crack, length a_0 . For this situation the residual stress distribution will be given by

$$\sigma_c \approx \frac{-E\epsilon}{(1-\nu)} \text{ for } t > x > (W - t) \quad (4)$$

and

$$\sigma_t \approx 0 \quad \text{for } t < x < (W - t) \quad (15)$$

For situations where the surface layers are a different material, the elastic constants in Eq. (4) refer to the surface material. In the absence of an applied stress, the residual stress will act to close the crack so that its surfaces are in contact. For example, it is expected that the crack surfaces will be in contact to a depth t , or for $t/a_0 > 1$, the crack will be completely closed. When a tensile stress is applied to the body the crack will begin to open until at a critical applied stress the crack surfaces will no longer be in contact. The primary intent in this paper is to consider situations when $t/a_0 < 1$ and in particular to derive the stress intensity factor (K_I) for this configuration. In this way, it will then be possible to determine the strengthening in terms of t/a_0 . In order to do this, however, it is necessary to compute the amount of crack closure as a function of the residual and applied stresses.

A. Crack Closure Analysis

A partially-closed surface crack is illustrated in Fig. 2. For the residual stress distribution being considered, the surface crack is assumed to open from its tip back to the surface under the action of an applied stress. This is reasonable when $t/a_0 < 1$, as considered in this analysis. It should, however, be noted that when $t/a_0 > 1$, the lower constraint at the surface would

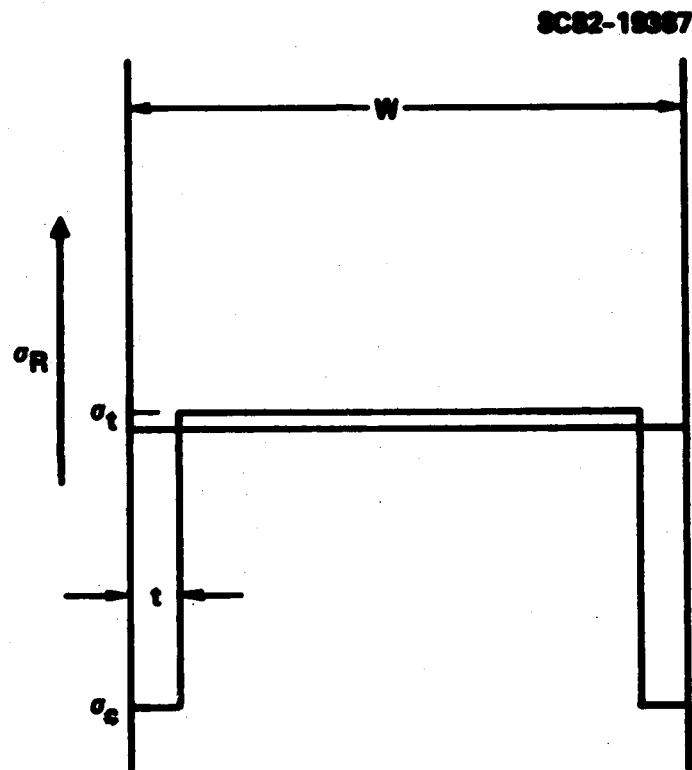


Fig. 2 Surface crack in semi-infinite plate with partial crack closure due to the surface compression.



probably lead to the crack opening in the opposite direction. For these situations, however, the strengthening should be simply given by Eq. (3).

It has been noted by other workers^(3,5,8,9) that the stress intensity factor at contact zone (left hand crack tip in Fig. 3) will be zero. It is then possible with this condition to determine the crack closure length (c). This procedure is relatively complex, but for this work a simple solution will be used that was derived by Barenblatt.⁽¹²⁾ This solution is strictly only valid for an internal crack in an infinite body but as will be shown later it gives a reasonable description of the closure length. In terms of Fig. 3 the closure distance is given by⁽¹²⁾

$$\frac{a}{a + (t - c)} = \cos \left[\frac{\pi \sigma_a}{2\sigma_c} \right] \quad (4)$$

where σ_a is the applied tensile stress. Using $2a = a_0 - t$, one obtains

$$c_1 = \frac{(1 + t_1) \cos \alpha - (1 - t_1)}{2 \cos \alpha} \quad (5)$$

where $c_1 = c/a_0$, $t_1 = t/a_0$ and $\alpha = \pi\sigma_a/2\sigma_c$. Equation (5) is illustrated in Fig. 3. It can be seen that the crack becomes completely open at a critical value of (σ_a/σ_c) which depends on (t_1) . As indicated earlier, the analysis is not expected to be valid as $t_1 > 1$. This is reflected in Eq. (5), which becomes independent of the applied stress for $t_1 = 1$. For values of $t_1 > 1$, it is simply assumed that the crack is completely closed until $\sigma_a = -\sigma_c$ and then it becomes completely open. It should also be noted that the use of Eq. (4) ignores the effect of the free surface of the closure length, this is expected to be important as $c_1 \rightarrow 0$. For these conditions, however, the crack will be almost completely open and provided the stress intensity factor solution approaches that of an open crack, the approximation should be reasonable.

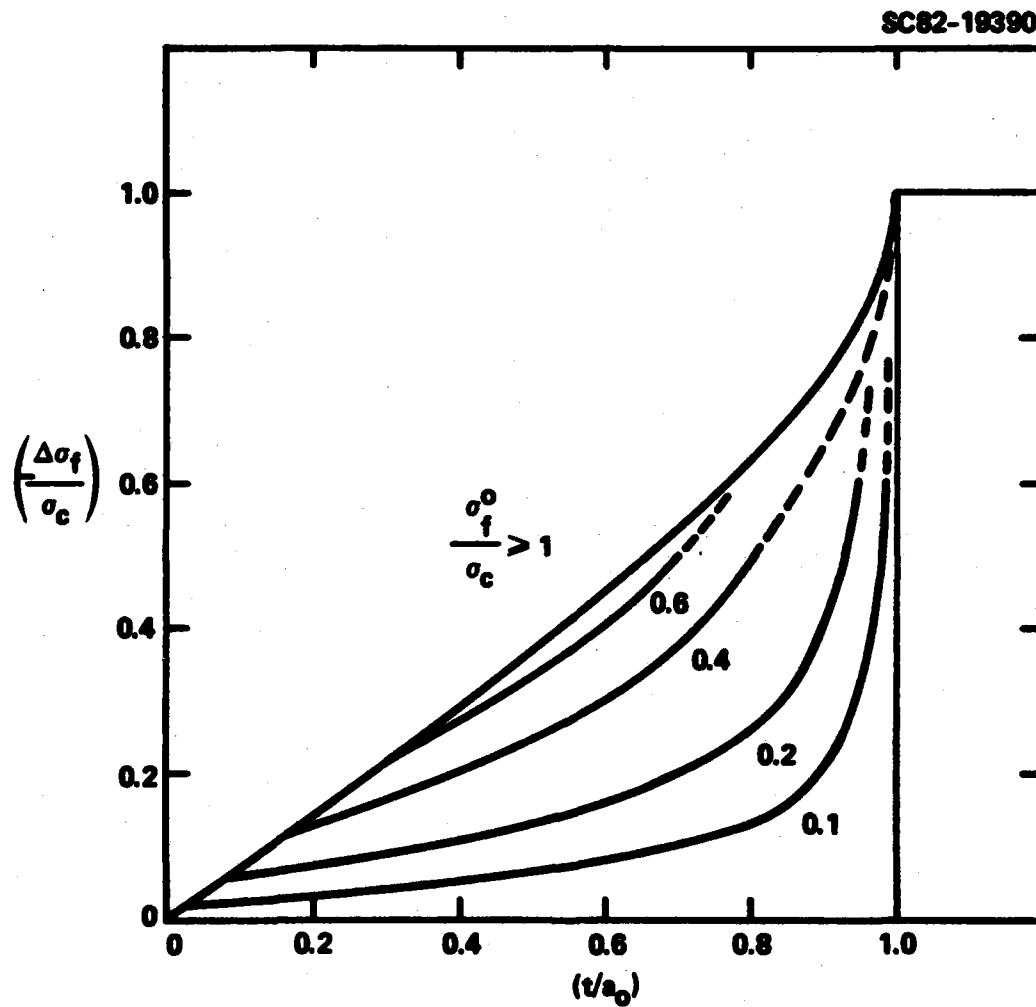


Fig. 3 Crack closure length as a function of the compressive zone depth and applied stress.



B. Calculation of Stress Intensity Factor

For a partially-closed internal crack, length $2a_0$, it has been shown that(2)

$$K_I = 2\left(\frac{a_0}{\pi}\right)^{1/2} (1 - c_1^2)^{1/2} \int_{c_1}^1 \frac{\sigma(x_1) x_1 dx_1}{\sqrt{[(1 - x_1^2)(x_1^2 - c_1^2)]}} \quad (6)$$

where $x_1 = x/a_0$ and $\sigma(x_1)$ is the prior stress acting along the plane of the crack. The coordinate axes are located so the plane of the crack lies along $y = 0$ and the center of the crack is at $x = 0$. In order to apply this solution to that of a surface crack, the effect of the free surface should be included. This is ususally accomplished by modifying the stress distribution, i.e.,(13)

$$K_I = 2\left(\frac{a_0}{\pi}\right)^{1/2} (1 - c_1)^{1/2} \int_{c_1}^1 \frac{\sigma(x_1) f(x_1) x_1 dx_1}{\sqrt{[(1 - x_1^2)(x_1^2 - c_1^2)]}} \quad (7)$$

where

$$f(x_1) = 1.2945 - 0.6857 x_1^2 + 1.1597 x_1^4 - 1.7627 x_1^6 + 1.5036 x_1^8 - 0.5094 x_1^{10} \quad (8)$$

For the residual stress distribution given by Eqs. (4) and (5) and an applied tensile stress, Eq. (7) can be re-written as

$$K_I = 2\left(\frac{a}{\pi}\right)^{1/2} (1 - c_1^2)^{1/2} \int_{c_1}^1 \frac{(\sigma_a + \sigma_c) f(x_1) x dx_1}{\sqrt{[(1 - x_1^2)(x_1^2 - c_1^2)]}} + \int_{t_1}^1 \frac{\sigma_a f(x_1) x_1 dx_1}{\sqrt{[(1 - x_1^2)(x_1^2 - c_1^2)]}} \quad (9)$$

Now if we substitute



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$$x_1^2 = c_1^2 - (1 - c_1^2) u^2 \quad (10)$$

and expand $f(x_1)$ in terms of u^2 , i.e.,

$$f(x_1) = \sum_{k=0}^5 a_{2k} u^{2k} \quad (11)$$

one obtains

$$K_I = 2 \left(\frac{a_0}{\pi} \right)^{1/2} (1 - c_1^2) \sum_{k=0}^5 a_{2k} \int_0^{t_2} \frac{u^{2k} (\sigma_a + \sigma_c) du}{\sqrt{(1 - u^2)}} + \int_{t_2}^1 \frac{u^{2k} (\sigma_a) du}{\sqrt{(1 - u^2)}} \quad (12)$$

where

$$t_2 = \frac{t_1^2 - c_1^2}{1 - c_1^2}^{1/2} \quad (13)$$

From standard integral tables

$$\int \frac{u^{2k} du}{(1 - u^2)^{1/2}} = \frac{(2k)!}{(k!)^2} \left[- (1 - u^2)^{1/2} \sum_{r=1}^k \frac{r! (r-1)! u^{2r-1}}{2^{2k-2r+1} (2r)!} + \frac{1}{2^{2k}} \sin^{-1} u \right] \quad (14)$$

The final solution for the stress intensity factor is given by

$$K_I = \sigma_c \left(\frac{a_0}{\pi} \right)^{1/2} (1 - c_1^2)^{1/2} \left[F_1(t_2) + F_2(c_1) \left(\frac{\sigma_a}{\sigma_c} + \frac{2}{\pi} \sin^{-1} t_2 \right) \right] \quad (15)$$

where

$$F_1(t_2) = \sum_{k=1}^5 - \frac{a_{2k} (2k)! (1 - t_2^2)^{1/2}}{2(k!)^2} \sum_{r=1}^5 \frac{r! (r-1)! t_2^{2r-1}}{2^{2k-2r+1} (2r)!} \quad (16)$$



and

$$F_2(c_1) = \sum_{k=0}^5 \frac{a_{2k} (2k)!}{(k!)^2 2^{2k}} \quad (17)$$

It can be shown that Eq. (15) agrees with several limiting cases. For example, in the absence of a residual stress

$$K_I = 1.1215 \sigma_a (\pi a_0)^{1/2} \quad (18)$$

in agreement for the solutions for a surface crack in an applied tensile stress field.⁽¹³⁾ For the condition when $-\sigma_a = \sigma_c$, ($c_1 = 0$)

$$K_I = \sigma_a (\pi a_0)^{1/2} \left[\frac{2}{\pi} \cos^{-1} t_1 \right] G(t_1) \quad (19)$$

The solution agrees with that derived for a uniform stress near a crack tip,⁽¹³⁾ where

$$G(t_1) = \frac{\pi F_1(t_2)}{2 \cos^{-1} (t_1)} \quad (20)$$

Finally for $\sigma_a = 0$ and σ_c is a tensile stress

$$K_I = \sigma_c (\pi a_0)^{1/2} \left(\frac{2}{\pi} \sin^{-1} t_1 \right) H(t_1) \quad (21)$$

where

$$H(t_1) = \frac{\pi F_1(t_2)}{2 \sin^{-1} (t_1)} \quad (22)$$

This solution agrees with previous solutions^(14,15) for $0 < t_1 < 1$, in which a surface crack has a uniform stress near the free surface.



In order to determine the condition for strengthening the fracture condition the fracture condition must be used, i.e., $K_I = K_C$. Using this condition and $K_C = 1.1215 \sigma_f^0 (\pi a_0)^{1/2}$ where σ_f^0 is the strength of the body in the absence of residual stress, Eq. (15) can be rewritten as

$$-\frac{\Delta\sigma_f}{\sigma_c} (1 - c_1)^{1/2} = \frac{F_1(t_2)}{F_2(c_1)} + \frac{2}{\pi} \sin^{-1} t_2 + \frac{\sigma_f^0}{\sigma_c} (1 - c_1^2)^{1/2} - \frac{1.1215 \sigma_f^0}{F_2(c_1) \sigma_c} \quad (23)$$

This equation is presented as Fig. 4 and will be discussed in the following section. In the analysis it was found that for $\sigma_f^0/\sigma_c > 1$, the crack will be completely open at failure and the value of $\Delta\sigma_f/\sigma_c$ depends only on t/a_0 . It was found, however, that as $c/a_0 \rightarrow 0$ in situations where $\sigma_f^0/\sigma_c < 1$, the analysis was in error and did not agree with the limiting cases. These problems are presumably a result of the approximate method for determining the closure distance. For values of $t/a_0 > 1$, it was simply assumed that $\Delta\sigma_f/\sigma_c = -1$.



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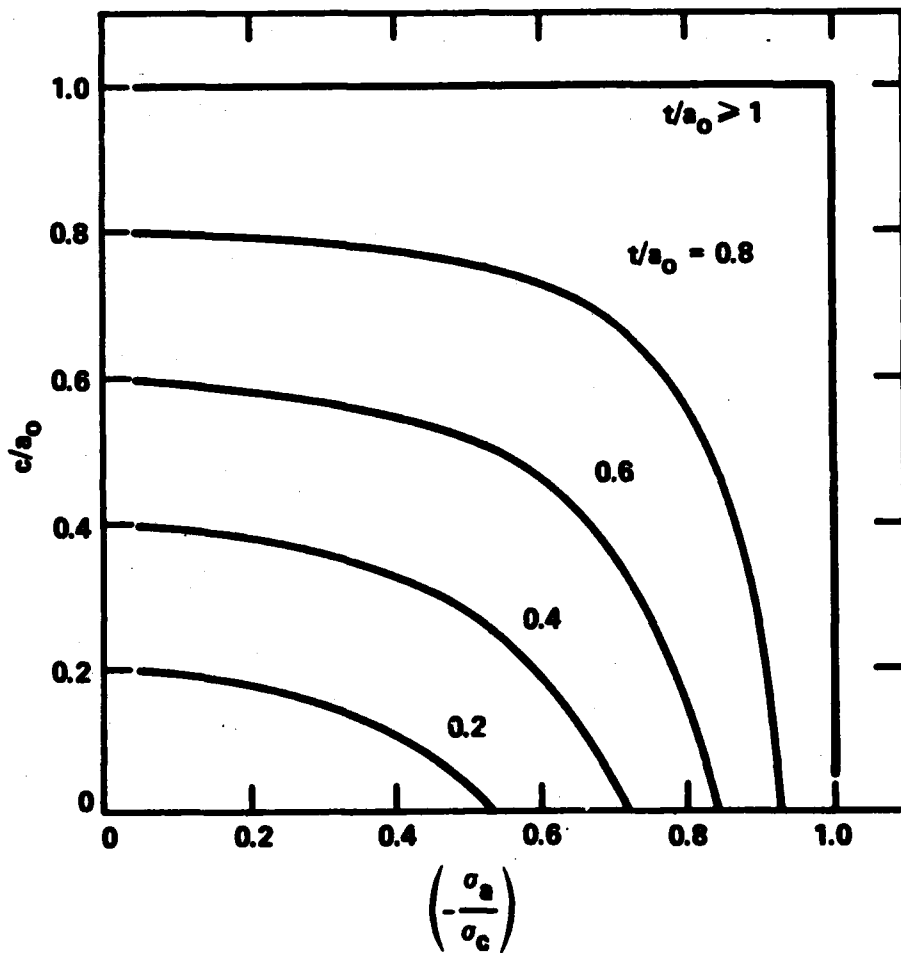


Fig. 4 Strengthening due to surface compression in a semi-infinite plate in terms of compressive stress.



III. DISCUSSION

The data presented as Fig. 4, have important consequences for optimization of compressive strengthening. For example, for a given value of σ_c , it is best to have a compressive surface layer that is at least as deep as the surface flaws. In many situations, however, this may not be possible, so for example, at a fixed value of t/a_0 , the basic strength of the body (σ_f^0) should be as high as possible. This could be accomplished by increasing the basic fracture toughness of the material. Alternatively decreasing the size of the surface flaws would increase σ_f^0 as well as increasing t/a_0 . The strength increase in terms of σ_f^0 is shown in Fig. 5, which allows us to consider the effect of varying σ_c for constant σ_f^0 . It is interesting to note here that increasing σ_c for situations where $t/a_0 < 1$ does lead to strengthening but the effect saturates as $\sigma_f^0/\sigma_c \rightarrow 0$. It should also be remembered that σ_c is not necessarily independent of t/a_0 . For example, increasing the compressive layer depth usually decreases σ_c . This effect can be seen for example, in Eq. (1). Therefore, in order to use Figs. 4 or 5 for a particular system the variation of σ_c with t/a_0 must be known and incorporated into the analysis.

Finally, although the production of surface compressive layers is expected to lead to strengthening for materials that fail from surface defects, it must be remembered that if internal flaws act as alternate failure origins, the potential strengthening discussed in this paper, would not be accomplished.

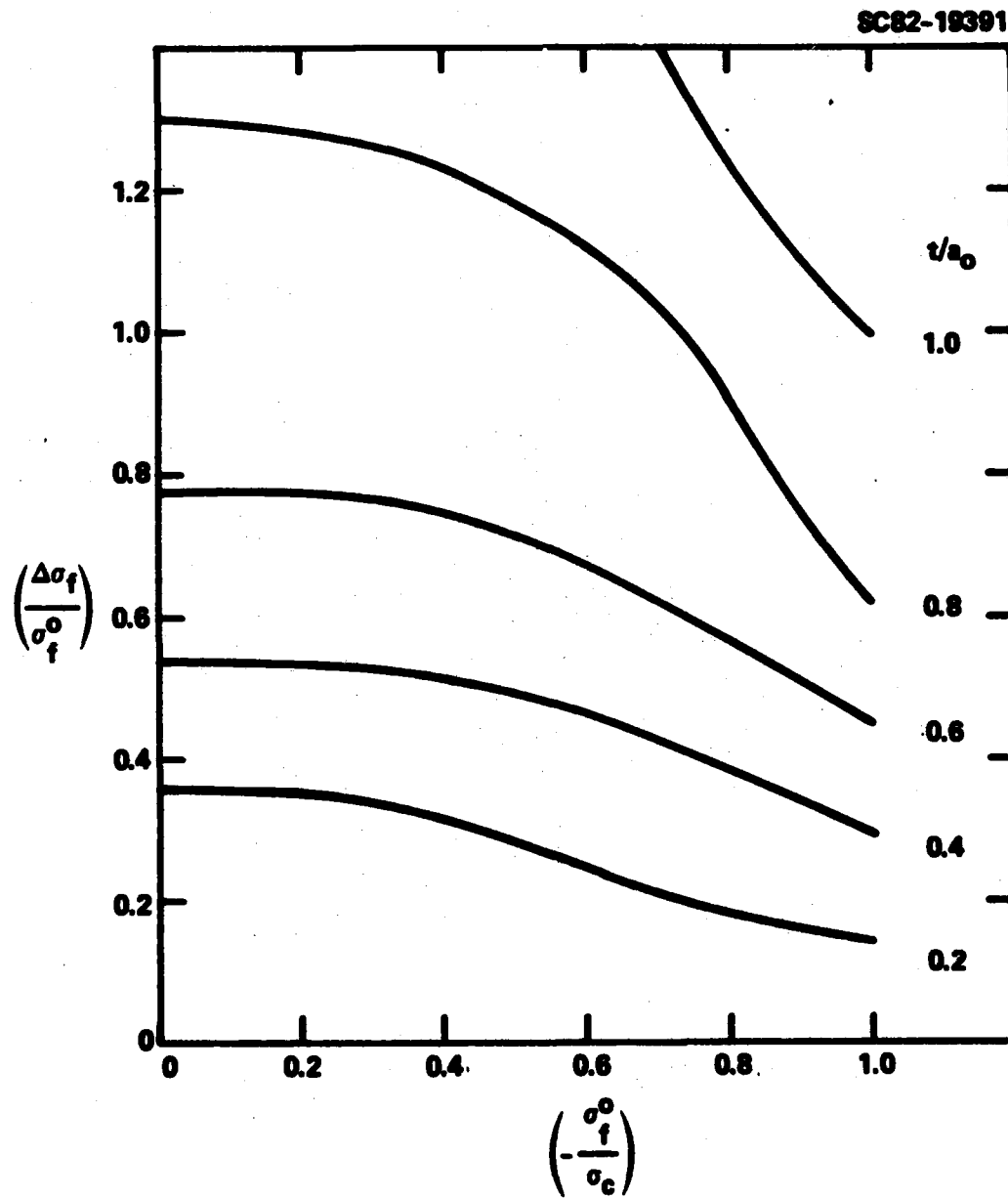


Fig. 5 Strengthening due to surface compression in a semi-infinite plate in terms of base strength of material.



IV. CONCLUSIONS

An approach has been put forward for predicting the strengthening of a brittle material, when it is subjected to a particular residual stress distribution. The approach involved the calculation of the amount of crack closure and the subsequent determination of the stress intensity factor for the particular configuration. For the cases where a critical surface crack is completely open at the failure condition, the strengthening simply depends on the magnitude of the compressive stress and the ratio of the compressive layer depth to flaw size. In particular, when this ratio > 1 , the maximum strengthening is obtained. For situations, however, where the surface crack is only partially open at failure, the amount of strengthening also depends on the basic strength of the material. For example, for a given surface compressive stress, the strengthening can be increased by increasing the base strength of the material. Alternatively, in situations where the base strength cannot be increased, the strengthening can be increased by increasing the magnitude of the compressive stress. This effect, however, saturates at high values of compressive stress. Finally, it was noted that the magnitude of the surface compressive stress depends on the process being used to induce the residual stresses and that failure from an alternate flaw population could reduce the optimum strengthening predicted in this work.

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TECHNICAL REPORT NO. 16

**TRANSFORMATION TOUGHENING: THERMODYNAMIC APPROACH TO
PHASE RETENTION AND TOUGHENING**

F.F. Lange



TRANSFORMATION TOUGHENING: THERMODYNAMIC APPROACH
TO PHASE RETENTION AND TOUGHENING

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INTRODUCTION

Stress-induced phase transformations can be used to significantly increase the fracture toughness and strength of brittle materials.¹⁻⁶ The ZrO_2 (tetragonal) \rightarrow ZrO_2 (monoclinic) transformation, which is accompanied by a 3-5% volume increase and a shear strain of $\sim 8\%$,^{7,8} has been used to demonstrate this fact. To use the transformation toughening concept, one must first retain the high temperature phase (e.g., $ZrO_2(t)$) by elastic constraint to temperatures below the unconstrained transformation temperature; that is, tetragonal ZrO_2 is the toughening agent. Experimental observations have shown that the retention of $ZrO_2(t)$ depends on the size of the transforming volume element, viz. a critical grain size or inclusion size must not be exceeded during fabrication. The work done by the loading system to stress-induce the $t \rightarrow m$ transformation in the vicinity of the crack front is responsible for increasing fracture toughness.

The object here is to review the thermodynamic approach⁶ to the conditions required to retain the toughening agent and its contribution to toughening. Although this approach is general for any fast transformation, the $t \rightarrow m$ transformation will be emphasized. Experimental observations will then be reviewed to compare with theory. Before this is started, four basic microstructures that can be fabricated will be reviewed to set the stage in our discussion, which ultimately relates thermodynamics, microstructures, and properties.



precipitated microstructures can be obtained in large single crystals by Scull melting, as demonstrated by Rice et al.,¹² and by sintering powders. The CSIRO Group (Garvie and co-workers)^{1,2} have pioneered this sintered microstructure in the $\text{ZrO}_2\text{-CaO}$ system, and the Case-Western Group (Hauer and students)³ in the $\text{ZrO}_2\text{-MgO}$ system. The sintered microstructures consist of large cubic grains (a result of high temperatures sintering) which contain the internal and grain boundary tetragonal precipitates. The volume fraction of the precipitates is governed by the alloying agent and the heat treatment schedule in the two-phase field.

A second microstructure, consisting of polycrystalline, single phase tetragonal ZrO_2 , can be fabricated by sintering composite $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ (< 3 m/o) powders in the tetragonal phase field, provided that the resulting grain size is less than the critical value (dependent on the Y_2O_3 content). Gupta et al.^{4,5} pioneered this microstructure. Here, neighboring grains constrain one another from the anisotropic transformation strains.

The third microstructure, pioneered by the author,⁶ is a two-phase, tetragonal/cubic polycrystalline material in which neighboring grains are either tetragonal or cubic. This microstructure is fabricated by sintering $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ composite powders in the two-phase, $t + c$ field. Here again, the tetragonal phase is retained only if the fabricated grain size does not exceed a critical value. The volume content of the tetragonal phase can be varied from 100% to 0% by changing the Y_2O_3 content from ~ 3 m/o to ~ 7 m/o.

The fourth microstructure is developed by incorporating ZrO_2 into a chemically compatible matrix phase to obtain a polycrystalline, two-phase material by sintering. The $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite system, pioneered by Claussen,¹³ is typical of such systems. Except for very dilute composites (< 10 v/o of the minor phase) on either end of the binary, the composite is itself the constraining matrix. Here, as with other two-phase ceramics, the volume fraction at which the minor phase becomes continuous depends on the dihedral angle. Although the minor phase is primarily located at three and four grain junctions, smaller second phase grains can be observed within the major phase grains indicative of entrapment during grain growth.

Combinations of the above 4 microstructures are possible.

To generalize, the critical inclusion (on grain) size required to retain the ZrO_2 in its tetragonal state depends on the amount and type of alloy added (e.g., Y_2O_3 , CaO , MgO , CaO , etc.) to ZrO_2 , the elastic modulus of the constraining matrix, and the temperature in question. The objective of the next section is to examine the end-point thermodynamics of the constrained transformation in order to put these general observations in an ordered perspective.

**CONDITIONS FOR PHASE RETENTION: THERMODYNAMICS OF A CONSTRAINED TRANSFORMATION (Ref. 6 - Part 1)**

The transformation thermodynamics of an isolated, spherical inclusion constrained by an elastic matrix can be viewed, to the first approximation, by examining the change in free energy (ΔG) between the initial, untransformed (tetragonal) state and its final, transformed (monoclinic) state; the transformation can only proceed if $\Delta G < 0$. Although the transformation must satisfy this initial to end-point condition, it should be noted that growth of a transforming nucleus which consumes the inclusion must also satisfy the condition $\Delta G < 0$ during all stages of growth. Thus, it should be recognized that initial to end-point thermodynamics only estimates transformation conditions, since it neglects "energy barriers" encountered by growing nuclei, viz. it neglects the effect of the initial nucleus size. Even without detailed knowledge of the transformation mechanics and the mechanics of surface phenomena accompanying the transformation, end-point thermodynamics can at least point a direction to uncover the transformation conditions.

For the case when no external stress state is applied to the system, the contribution to the end-point free energy change includes 3 terms: the chemical free energy change (ΔG_c), differential strain energy (ΔU_{se}), and energy changes (ΔU_s) associated with interfacial surfaces and surface phenomena accompanying the transformation. The chemical free energy, ΔG_c , is most dependent on temperatures and alloy content. As indicated in Fig. 1, ΔG_c is negative below $\sim 1200^\circ\text{C}$ for the $\text{ZrO}_2(\text{t}) \rightarrow \text{ZrO}_2(\text{m})$ reaction. Below $\sim 1200^\circ\text{C}$, its absolute value, $|\Delta G_c|$, increases with decreasing temperature. Figure 1 also shows that alloying with Y_2O_3 (up to ~ 3.5 m/o) decreases $|\Delta G_c|$ at, e.g., room temperature. Thus, $|\Delta G_c|$ is inversely dependent on temperature and alloy content.

Since the transformation involves a volume change and shear strains, which are constrained by the matrix, a state of stress will arise within both the transformed inclusion and the surrounding matrix. A differential strain energy (ΔU^0) thus arises from the constrained stress state associated with the transformation. It can be shown that for a given transformation, the magnitude of ΔU^0 is proportional to the stiffness of the matrix,⁶ i.e., the greater the elastic modulus of the constraining matrix, the greater ΔU^0 . It should be noted that ΔU^0 is always positive. Residual stresses associated with the initial, untransformed state must also be included in the differential strain energy. Such residual stresses can arise as a result of differential thermal expansion before the inclusion attempts to transform. When these residual stresses are included, the total differential strain energy per unit volume can be expressed as⁶



$$\Delta U_{se} = \Delta U_{se}^0 + \sigma_{ij}^r \epsilon_{ij}^r + \sigma_{ij}^r \epsilon_{ij}^t \quad (1)$$

where σ_{ij}^r and ϵ_{ij}^r are the residual stress and strain components associated with the untransformed state, σ_{ij}^t are the stress components associated with the transformation, and ϵ_{ij}^t are the unconstrained transformation strains. ΔU_{se}^0 is the strain energy only associated with the transformation, i.e.,

$$\Delta U_{se}^0 = \frac{1}{2} \sigma_{ij}^t \epsilon_{ij}^t$$

Equation (1) illustrates that the residual strains either increase or decrease the strain energy, depending on their sense. For example, if the transformation strains are tensile and the initial residual strains are tensile, the strain energy is diminished. If, on the other hand, the residual strains have a different sense than those associated with the transformation, then the total strain energy differential is increased. As will be shown next, the magnitude of ΔU_{se} is one factor that controls the constrained transformation temperature.

Before discussing the details and effects of the surface phenomena term, ΔU_s , we can sum the three terms to show that the constrained transformation temperature is lower than the unconstrained transformation temperature:

$$\Delta G_{t \rightarrow m} = -|\Delta G_c| + \Delta U_{se} + \Delta U_s \quad (2)$$

Since the transformation will not proceed unless $\Delta G_{t \rightarrow m} < 0$, the condition for transformation is

$$|\Delta G_c| > \Delta U_{se} + \Delta U_s \quad (3)$$

That is, the contribution of the differential strain energy is to change the transformation temperature. Thus, retention of tetragonal ZrO₂ to, e.g., room temperature is possible in a constrained state, provided that the differential strain energy is sufficiently large.

Although ΔU_{se} is an important term in changing the transformation temperature, the summation of ΔG_c and ΔU_{se} cannot result in a size effect, i.e., both terms have the same dependence on the volume (or size) of the transforming inclusion. As will be shown, the size effect resides in the surface term, ΔU_s .

Three surface phenomena are known to accompany the ZrO₂(t) \rightarrow ZrO₂(m) transformation: interfacial surface change,



twinning, and microcracking. Each will contribute to the differential surface energy and, as will be shown, twinning and microcracking will both alter the differential strain energy.

As Garvie¹⁴ has pointed out, both the surface area and the interfacial surface energy per unit area will change during transformation. Thus, the differential interfacial surface energy per unit volume will have the form

$$\Delta U_{IF} = \frac{A_M \gamma_M - A_T \gamma_T}{V} = \frac{6(\gamma_M - \gamma_T s_g)}{D} \quad (3)$$

A_T and A_M are the interfacial surface areas of the tetragonal and monoclinic inclusion, γ_T and γ_M are their respective interfacial surface energies per unit area, and $s_g = A_T/A_M$. For simplicity, the transformed particle is assumed to be a sphere with a volume = $(\pi/6)D^3$ and a diameter D . Thus, when Eqs. (3) and (2) are combined, the interfacial surface term introduces a size effect such that when $\Delta G_c < 0$, only those size inclusions with

$$D > D_c^{IF} = \frac{6(\gamma_M - \gamma_T s_g)}{|\Delta G_c| - \Delta U_{se}} \quad (4)$$

can undergo transformation and lower the system's free energy. As shown by Eq. (4), this size effect only occurs at temperatures where $|\Delta G_c| > \Delta U_{se}$.

It will now be shown that the size effects due to twinning and/or microcracking will occur at temperatures where $|\Delta G_c| < \Delta U_{se}$, i.e., these size effects are first encountered upon cooling from the fabrication temperature.

Both twinning (or the formation of invariant planes by the moving transformation front) and microcracking not only introduce new surface energy, but they also relieve a portion of the constraint and thus decrease the differential strain energy. Twinning helps relieve constraint caused by the shape (shear) change associated with the transformation and thus reduces the shear portion of the strain energy by a factor $(1 - f_T)$. Microcracking relieves some constraint due to the volume change and thus reduces the strain energy by a factor $(1 - f_c)$. It can be shown that the summation of the reduced differential strain energy and the differential surface energy as expressed in energy per unit volume for these two surface phenomena are

$$\Delta U_{se} f_T + \frac{6\gamma_T f_T}{D} \quad \text{for twinning} \quad (5)$$



and

$$\Delta U_{se} f_c + \frac{6\gamma_c s_c}{D} \quad \text{for microcracking} \quad (6)$$

where $0 < f < 1$, $s_T = A_T/A_m$, $s_c = A_c/A_m$, A_T = total area of twins, A_c = total area of crack(s), and γ_T and γ_c are the respective surface energies per unit area for twin boundaries and microcrack surfaces.

Combining Eqs. (5) and (6) with the chemical free energy change and setting $\Delta G = 0$, one obtains the critical inclusion size for transformation and twinning:

$$D_c^T = \frac{6(\gamma_T s_T + \gamma_m - \gamma_c s_c)}{|\Delta G_c| - \Delta U_{se} f_T} \quad (7)$$

which only occurs at temperatures where $|\Delta G_c| > \Delta U_{se} f_T$, and for transformation and microcracking:

$$D_c^c = \frac{6(\gamma_c s_c + \gamma_m - \gamma_c s_c)}{|\Delta G_c| - \Delta U_{se} f_c} \quad (8)$$

which only occurs at temperatures where $|\Delta G_c| > \Delta U_{se} f_c$.

If the transformation were accompanied by all three surface phenomena, then the critical size becomes

$$D_c^{T,c} = \frac{6(\gamma_T s_T + \gamma_c s_c + \gamma_m - \gamma_c s_c)}{|\Delta G_c| - \Delta U_{se} f_T} \quad (9)$$

Since Eqs. (4), (7), (8), and (9) are defined for the condition $\Delta G = 0$, they therefore define a phase boundary in size/temperature space which not only summarize the constrained transformation temperature, but also indicate the accompanying surface phenomena. Thus, when these critical size relations are normalized by the critical size relation for the constrained transformation ($\Delta U_{se} = 0$), viz.

$$D_{uc} = \frac{6(\gamma_m - \gamma_c s_c)}{|\Delta G_c|} \quad (10)$$

then D_c/D_{uc} can be plotted against $\Delta U_{se}/|\Delta G_c|$ as shown in Fig. 2. Without knowing the values of f_T , f_c , s_T , s_c , etc. but knowing their relative magnitudes e.g., $f_c > f_T$, $s_T > s_c$, and $\gamma_c > \gamma_T > \gamma_m - \gamma_c s_c$, one can obtain the phase fields shown in Fig. 2.

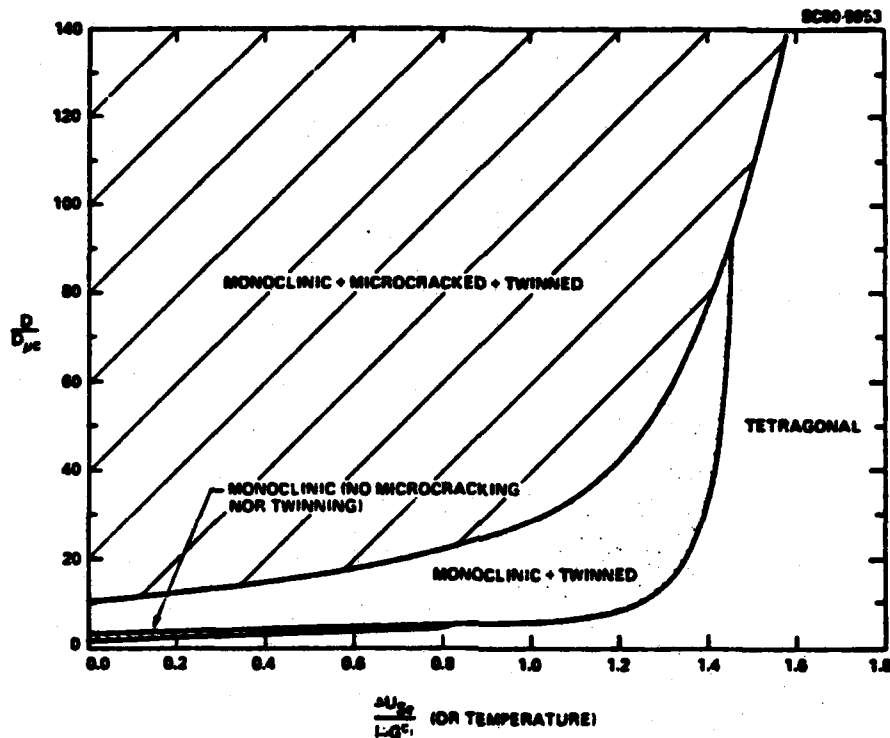


Fig. 2. Phase diagram resulting from surface phenomena accompany transformation.⁶

As detailed elsewhere,⁶ the phase diagram shown in Fig. 2 is important to the fabricator who needs to retain the tetragonal phase upon cooling to room temperature. First, it illustrates how surface phenomena that accompany the transformation result in a size effect. Second, it illustrates how the critical size depends on temperature, differential strain energy, and differential chemical free energy. The latter two can be modified by the fabricator to increase the critical size and thus relax the fabrication constraint of grain growth that accompanies sintering and/or heat treatment.

Three examples can be cited where the critical size has been changed in accordance with the thermodynamics leading to Fig. 2. First,⁶ alloying ZrO_2 with Y_2O_3 lowers $|\Delta G_c|$ at room temperature, up to additions of ~ 3.5 m/o, and Y_2O_3 thus should increase the critical grain size. Figure 3 shows this effect. Second, increasing the elastic modulus of the constraining matrix, e.g., by incorporating ZrO_2 into Al_2O_3 ($E_{Al_2O_3} = 400$ GPa, $E_{ZrO_2} = 200$ GPa), should increase the critical size. As shown in Table 1,¹⁵ the critical grain size with Al_2O_3/ZrO_2 constraining matrix is much larger than for pure ZrO_2 and depends on the composite's modulus. Third, one can use both alloying and increased elastic modulus to



increase the critical size. This is demonstrated by adding 2 to 3 m/o Y₂O₃ to the ZrO₂ and using Al₂O₃ as the constraining matrix. Here the critical size is raised above 1 μ m for all composite compositions in the Al₂O₃-ZrO₂ binary.⁶ That is, the use of Y₂O₃ permits one to fabricate Al₂O₃/ZrO₂(t) composites with much larger volume fractions of ZrO₂(t) without attempting to maintain ZrO₂(t), grain sizes < 0.5 μ m.

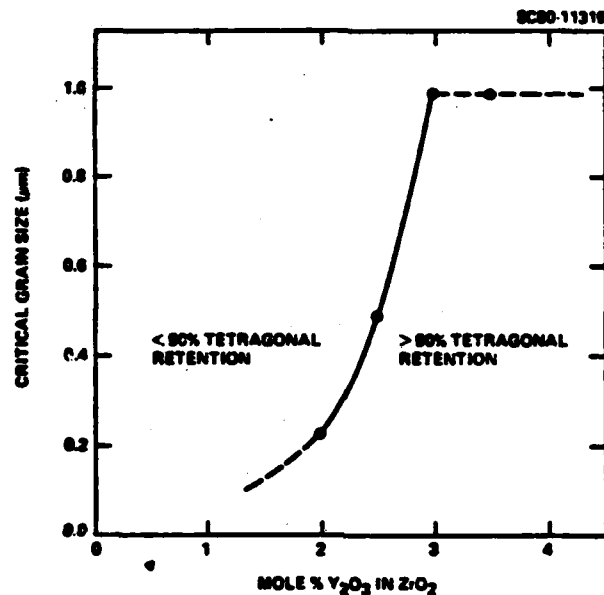


Fig. 3. Critical grain size vs Y₂O₃ content.⁶

Table 1. Critical Grain Size for Al₂O₃/ZrO₂ Composites¹⁵

Vol Fraction ZrO ₂	Heat Treatment		Critical Grain Size (μm)
	Temp (°C)	Time (h)	
0.05*	1650	12	>2.3
0.10	1650	4	1.35
	1650	8	1.35
	1650	12	1.41
0.15	1650	4	0.85
	1650	8	0.84
	1650	12	0.85
0.20**	1650	4	0.74

*Monoclinic ZrO₂ not detectable by x-ray diffraction.

**Longer heat treatment produced too much monoclinic ZrO₂ for reliable results.



WORK TO STRESS-INDUCE THE TRANSFORMATION

Before examining the fracture toughness contribution, let us first examine the work required to induce a constrained transformation. Again we will consider a spherical inclusion within an elastic matrix. If the stress state (σ) applied by external loads is of the same sense to the transformation strains, a sufficient stress can induce the transformation. Taking the $\text{ZrO}_2(\text{t}) \rightarrow \text{ZrO}_2(\text{m})$ transformation as an example, an applied triaxial tensile stress will unconstrain the volume increase associated with the transformation. As shown by Eshelby,¹⁶ the work per unit volume of transforming material done by the loading system is given by

$$W = \sigma_{ij}^2 c_{ij}^t \quad (11)$$

where c_{ij}^t are the components of the unconstrained transformation strain tensor. That is, the potential energy of the loading system is lowered by WV , where V is the transformed volume.

The end-point thermodynamics of this situation can be expressed as (below 1200°C for ZrO_2)

$$\Delta G_{t \rightarrow m} = -|\Delta G_c| + \Delta U_{se} f + \frac{6\gamma_{yg}}{D} - W \quad (12)$$

where $(1 - f)$ is the strain energy reduction due to the surface phenomena that relieves stress, and γ_{yg} are the sum of the surface energy terms for the surface phenomena accompanying the transformation. The minimum work required to stress-induce the transformation is determined when $\Delta G_{t \rightarrow m} = 0$,

$$W = -|\Delta G_c| + \Delta U_{se} f + \frac{6\gamma_{yg}}{D} \quad (13)$$

Eq. (13) shows that the work per unit volume required to induce the transformation is inversely proportioned to the inclusion size. If we multiply Eq. (13) by the volume of the transforming inclusion ($V = \frac{\pi}{6}D^3$), we can express the total work for transformation as

$$WV = -(|\Delta G_c| - \Delta U_{se} f) \frac{\pi}{6} D^3 + \pi \gamma_{yg} D^2 \quad (14)$$

This function is shown in Fig. 4, illustrating that the minimum work required to stress-induce the transformation is maximized when



BASIC MICROSTRUCTURES

The $\text{ZrO}_2\text{-Y}_2\text{O}_3$ binary system^{9,10,11} (Fig. 1) will be used to illustrate how 3 of the 4 basic microstructures that include the tetragonal ZrO_2 toughening agent are fabricated. As shown, Y_2O_3 forms a solid solution with ZrO_2 ($\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$) to reduce the $t \rightarrow m$ transformation temperature from $\sim 1200^\circ\text{C}$ for pure ZrO_2 to $\sim 600^\circ\text{C}$ for the eutectoid composition containing ~ 3.5 m/o Y_2O_3 .^{*} Additions of > 7 m/o Y_2O_3 stabilize the cubic structure to room temperature.

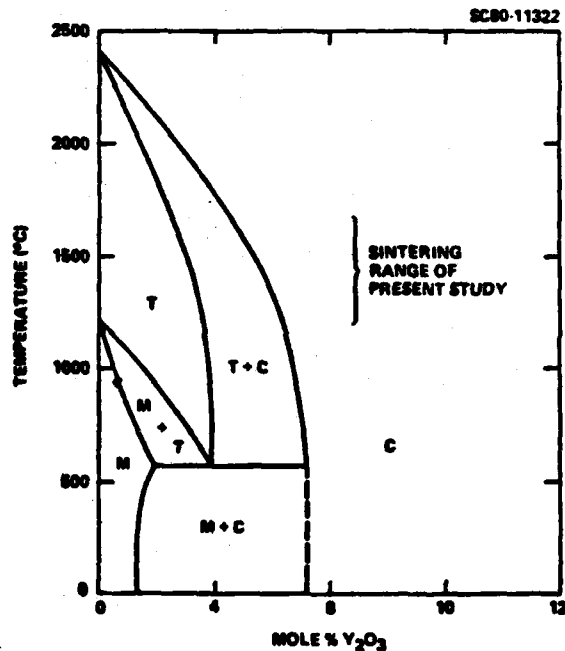


Fig. 1. $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system.^{9,10,11}

One microstructure that can be produced is obtained by fabricating ZrO_2 containing ~ 3 to 7 m/o Y_2O_3 in the high temperature cubic phase field, and then quenching into the two-phase (tetragonal + cubic) field to precipitate tetragonal inclusions from the cubic matrix. If the inclusions do not grow to exceed a critical size, the two-phase material can be cooled to room temperature to retain the inclusions in their tetragonal structure. Such

^{*}m/o = mole %; v/o = volume %.



$$D = D_{\max} = \frac{4\gamma r}{|\Delta G_c| - \Delta U_{ss} f} \quad (15)$$

Figure 4 also illustrates that no work is required to induce the transformation when $D = D_c$, i.e., the constrained transformation is spontaneous without an applied stress when $D > D_c$. Comparing Eq. (15) with those relations derived for the critical inclusion size for spontaneous transformation, one obtains a relation between D_{\max} and D_c :

$$D_{\max} = \frac{2}{3} D_c \quad (16)$$

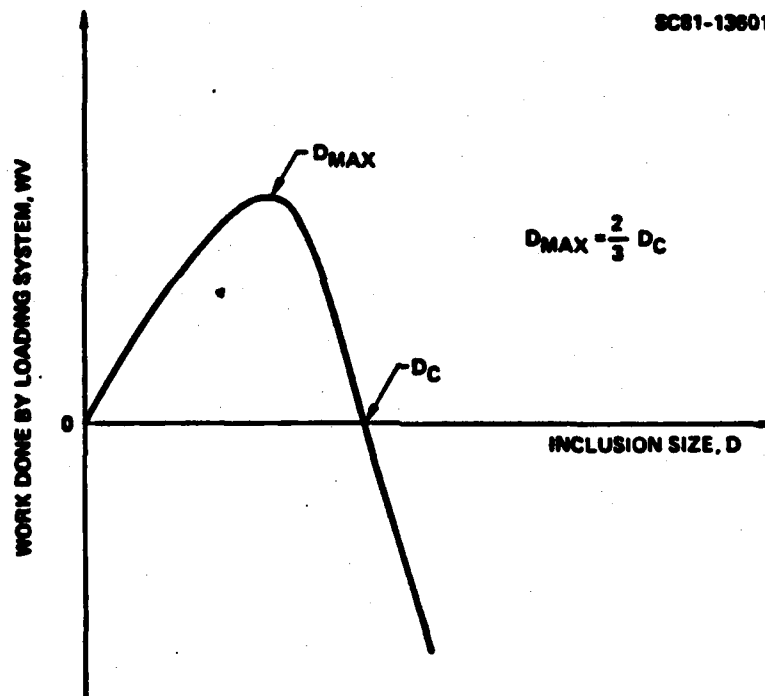


Fig. 4. Work done vs inclusion size.

Thus when the various surface phenomena that accompany the constrained transformation are incorporated into the end-point thermodynamics, one not only obtains a critical size effect for an unstressed, spontaneous transformation as illustrated in the last section, but also an inclusion size which maximizes the work required to stress-induce the transformation.

CONTRIBUTION TO FRACTURE TOUGHNESS⁶

The crack shielding approach to fracture toughness, which is also in a state of theoretical development, will not be reviewed here. This approach attempts to calculate the stress at the crack front to induce the transformation and then the stress-intensity solution of the crack shielded by the compressive stress field arising from the transformed material adjacent to the crack surfaces. Readers are referred to Evans et al.¹⁷ The approach outlined here concerns the thermodynamics of stress-induced transformation and crack extension.

Consider a pre-existing crack loaded in normal tension located in a material containing constrained inclusions of tetragonal ZrO₂. Under a sufficient load, the tensile and shear stresses at the crack front unconstrained the inclusions to cause them to transform. The loading system, through the crack's stress field does work during this stress-induced transformation. If crack extension were to occur and material transformed by the stress field were to remain in its transformed state once the stress field of the crack has moved on, then the work required for the transformation would be lost to the fracture process. That is, the stress-induced transformation contributes to increasing fracture toughness. The question is, how large is this contribution and under what conditions can this contribution be optimized.

From a thermodynamic view point, material adjacent to the crack front that stays in its transformed state once the crack's stress field is removed must be in a state of lower free energy relative to its initial constrained tetragonal state. Using the Irwin¹⁸ approach, i.e., where one determines the work to close a crack by a unit length, we can calculate the work required to retransform material adjacent to the crack front back to its tetragonal state and the work to close the crack.

Let us consider a crack under fixed grip conditions which has stress induced and then transverses an inclusion. The residual strain energy associated with the inclusion is $\Delta U_{se} f$, where ΔU_{se} is the strain energy change associated with transformation, and $(1 - f)$ is that portion of the strain energy relieved by the traversing crack. One might imagine that inclusions closer to the newly formed crack surface contain less strain energy than those far from the free surface. The first force field we apply reverts the fractured inclusion back to its tetragonal state. The work per unit volume performed by this first force field is

$$W = |\Delta G_c| - \Delta U_{se} f$$

where $|\Delta G_c|$ is the change in chemical free energy for the monoclinic to tetragonal transformation. One can see that the more



the inclusion is unconstrained by the fracture process, the smaller ΔU_{sef} and the greater the work. The total work done on all inclusion with the crack tip volume ($2RAA$) is

$$\Delta W_c = 2RAAV_1W = 2RV_1(|\Delta G_c| - \Delta U_{sef})AA \quad (17)$$

V_1 is the volume fraction of inclusion; R is the radius of the transformed zone adjacent to the crack front.

Once the inclusions are reverted to their tetragonal state, the strain energy associated with their transformed state disappears, and the crack now looks like an ordinary crack in a two-phase material. At this point, the second force field is applied to close the crack. As defined by Irwin,¹⁸ the critical work performed in this operation is

$$\Delta W_c = G_o AA \quad (18)$$

where G_o is the critical strain energy release rate for the composite material without the transformation phenomenon.

The total work for crack closure per unit crack length which also reverts the inclusions to their initial tetragonal state is thus

$$\frac{\Delta W}{AA} = G_c = G_o + 2RV_1(|\Delta G_c| - \Delta U_{sef}) \quad (19)$$

or, expressed as the critical stress intensity factor for the transforming composite,

$$K_c = \left(\frac{E_c G_c}{(1-\nu_c^2)} \right)^{1/2} = \left(K_o^2 + \frac{2RV_1 E_c (|\Delta G_c| - \Delta U_{sef})}{(1-\nu_c^2)} \right)^{1/2} \quad (20)$$

This result shows that the contribution of the stress-induced transformation is proportional to the volume fraction of the tetragonal phase (V_1), the elastic modulus of the composite (E_c), the difference between the chemical free energy change and the residual strain energy ($|\Delta G_c| - \Delta U_{sef}$), and the size of the transformation zone (R).

Experimental results for each of these factors will be reviewed in the next section.



FRACTURE TOUGHNESS: EXPERIMENTAL

Volume Fraction of Retained Tetragonal ZrO₂

Two different series of materials have been fabricated to investigate the effect of volume fraction of the retained tetragonal phase on fracture toughness. The first series was fabricated in the ZrO₂-Y₂O₃ system in which the Y₂O₃ content was increased from 2.5 m/o to 7.5 m/o in order to traverse the tetragonal/cubic phase field in Fig. 1. Figure 5 illustrates K_{IC} vs Y₂O₃ content which can be transformed directly to K_{IC} vs V_t (ZrO₂(t)) from XRD analysis of these two-phase materials.⁶ As illustrated, K_{IC} increases with increasing volume content of ZrO₂(t).

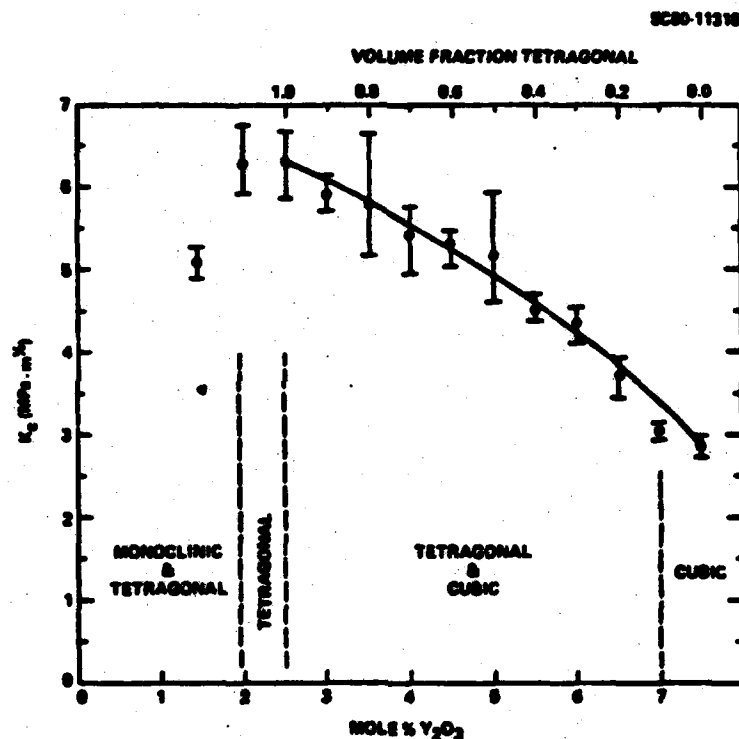


Fig. 5. K_{IC} for ZrO₂(t)/ZrO₂(c) composites.⁶

The second series was fabricated in the ZrO₂-Al₂O₃ system from one end member to the other. Y₂O₃ (2 m/o) was incorporated into the ZrO₂ in order to increase the critical grain size and allow complete retention of ZrO₂(t) to volume fraction up to ~ 60 v/o ZrO₂. Again, up to ~ 60 v/o ZrO₂, toughness increases with increasing v/o of ZrO₂(t), as shown in Fig. 6. Figure 6 also illustrates the toughness of the Al₂O₃/ZrO₂ (cubic) composite series in which 7.5 m/o Y₂O₃ was incorporated with the ZrO₂. For this series, toughness decreases from one end-member to the other.

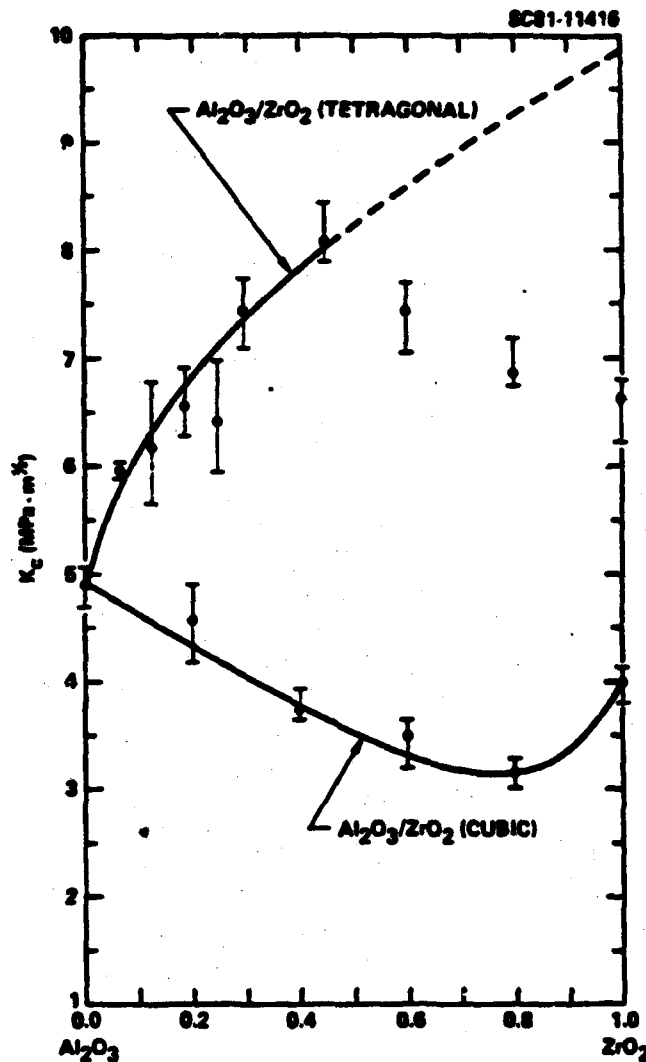


Fig. 6. K_c for $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites.⁶

Without the Y_2O_3 addition to ZrO_2 , tetragonal ZrO_2 can only be completely retained in the Al_2O_3 matrix to volume fractions ranging between 10 to 15 v/o ZrO_2 . For such a series, the K_c vs volume fraction data show a maximum at approximately the same volume fraction which maximizes the tetragonal phase.¹⁶

Elastic Modulus of Composite

Comparing the data shown in Figs. 5 and 6, one can see that at comparable volume fractions (< 50 v/o $\text{ZrO}_2(\text{t})$) more is gained with the high modulus $\text{Al}_2\text{O}_3/\text{ZrO}_2$ constraining matrix. For example, at 30 v/o $\text{ZrO}_2(\text{t})$ the toughness increase for the $\text{ZrO}_2(\text{c})/\text{ZrO}_2(\text{t})$



composite is $\sim 1.5 \text{ MPa} \cdot \text{m}^{1/2}$, whereas in the $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{t})$ composite the gain is $\sim 2.5 \text{ MPa} \cdot \text{m}^{1/2}$. Detailed comparison with theory is difficult, since all other factors have not been held constant. For example, the end-point solid-solution for the ZrO_2 in the $\text{ZrO}_2(\text{c})/\text{ZrO}_2(\text{t})$ composites is $\sim 3 \text{ m/o Y}_2\text{O}_3$, whereas it is $2 \text{ m/o Y}_2\text{O}_3$ in the $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{t})$ series.

Chemical Free Energy Change⁶

The magnitude of $|\Delta G_c|$ for the $\text{ZrO}_2(\text{t}) \rightarrow \text{ZrO}_2$ transformation decreases with increasing temperature and increasing alloy content. The effect of temperatures on K_c for a single phase $\text{ZrO}_2(\text{t})$ (+ 2 m/o Y_2O_3) and three $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{t})$ composites is shown in Fig. 7. As predicted by theory (Eq. (20)), K_c decreases with increasing temperature. When these data are combined with the known property data (E_c , K_0 and V_1) and Eq. (20) is used to calculate $(|\Delta G_c| - \Delta U_{\text{sef}})$ vs temperature, the slope of the function with respect to temperature is nearly identical to that of pure ZrO_2 .¹⁹ Also, the temperature where $(|\Delta G_c| - \Delta U_{\text{sef}}) = 0$ falls within the range of 680°C to 900°C , which is the expected range for $\text{t} \rightarrow \text{m}$ transformation of $\text{ZrO}_2 + 2 \text{ m/o Y}_2\text{O}_3$ (i.e., the temperature where $|\Delta G_c|$ for this composition is zero). These correlations are shown in Table 2. To obtain this agreement, the value of R used in Eq. (20) was chosen as the size of the $\text{ZrO}_2(\text{t})$ grains. This reasonable correlation suggests that $\Delta U_{\text{sef}} = 0$ and $R =$ the grain size of $\text{ZrO}_2(\text{t})$ inclusion. If one believes that these two correlations are not fortuitous, then it suggests that those grains closer to the crack surface contribute the most to the toughening and that the size of this most important transformation zone is equal to the grain size.

Table 2. Values Used to Analyze K_c vs Temperature Data⁶

MATERIAL	K_c ($\text{MPa} \cdot \text{m}^{1/2}$)	K_0 ($\text{MPa} \cdot \text{m}^{1/2}$)	$(\Delta G_c - \Delta U_{\text{sef}})$ ($\text{MJ} \cdot \text{m}^{-3}$)	E_c (GPa)	ν_c	V_1	R (μm)	$3(\Delta G_c - \Delta U_{\text{sef}})$		T_0 ($^\circ\text{C}$)
								$\frac{dT}{d(\Delta G_c - \Delta U_{\text{sef}})}$	$\frac{dT}{d(\Delta G_c - \Delta U_{\text{sef}})}$	
$\text{Al}_2\text{O}_3/29.3 \text{ m/o ZrO}_2$ (+2 m/o Y_2O_3) (Hot Pressed)	7.45	4.10	100	203	0.25	0.793	0.90	-0.29		680
$\text{Al}_2\text{O}_3/29 \text{ m/o ZrO}_2$ (+2 m/o Y_2O_3) (Sintered)	6.83	4.10	100	203	0.25	0.29	1.53	-0.27		730
$\text{Al}_2\text{O}_3/46 \text{ m/o ZrO}_2$ (+2 m/o Y_2O_3) (Hot Pressed)	6.30	3.70	100	205	0.25	0.45	1.10	-0.21		900
ZrO_2 (+2 m/o Y_2O_3) (Hot Pressed)	6.71	3.00	100	207	0.25	1.00	0.35	-0.24		820
Average of four materials								-0.25		765
ZrO_2 (pure) ¹⁹								-0.25		1000
$29.65 \text{ m/o Al}_2\text{O}_3, 1.50 \text{ m/o ZrO}_2 + 2 \text{ m/o Y}_2\text{O}_3$ ^{9,10}										680 - 820 C

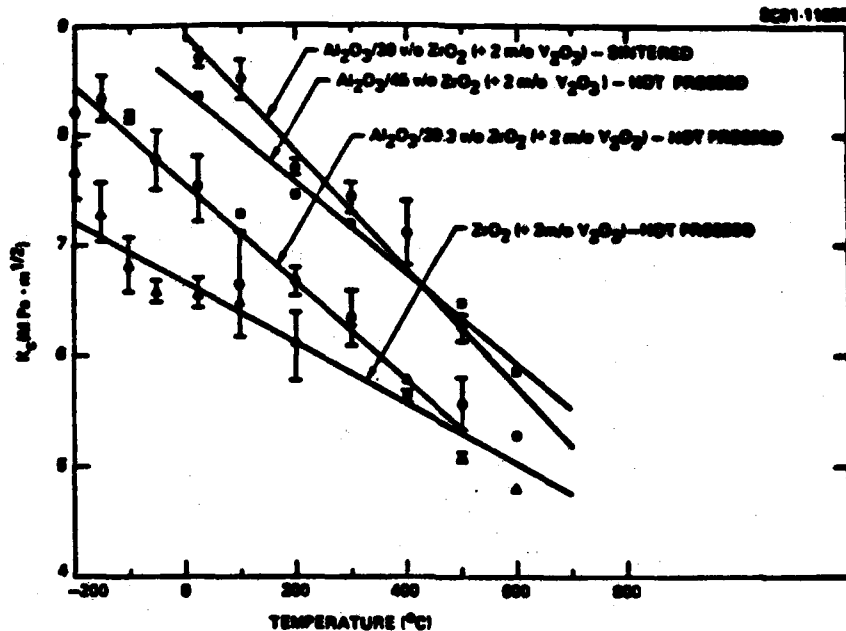


Fig. 7. K_{IC} vs temperature.⁶

The second way to change the magnitude of ΔG_c is to change the alloy content. Additions of CeO_2 were chosen, since the tetragonal phase field extends to ~ 20 m/o CeO_2 relative to the smaller phase field in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ binary. Composites containing $\text{Al}_2\text{O}_3/30$ v/o ZrO_2 (+ CeO_2) were fabricated by sintering in air. The mole % of CeO_2 was varied in 1 m/o increments between 6 m/o and 23 m/o CeO_2 . Tetragonal ZrO_2 was the only ZrO_2 phase for CeO_2 contents > 12 m/o. As shown in Fig. 8, K_{IC} decreases with increasing CeO_2 alloying addition as predicted from Eq. (20). If one extrapolates this data to 0 m/o CeO_2 , it suggests a value $K_{IC} = 10.3 \text{ MPa}\cdot\text{m}^{1/2}$ for these composite ($\text{Al}_2\text{O}_3/30$ v/o $\text{ZrO}_2(t)$) without the alloying addition.

Size of Transformation Zone

Various indirect and direct (thin foil, EM) observations suggest that the size of the transformation zone is $< 5 \mu\text{m}$ at room temperature. The above theory suggests that those inclusions closer to the fracture surface are less constrained after transformation and crack extension and thus contribute most to work loss during fracture. For this reason, this author has suggested that $R = D$. In addition, Section 4 strongly suggests that the work done per inclusion can be maximized by fabricating a material in which $D = 2/3 D_c$. For these reasons, an $\text{Al}_2\text{O}_3/25$ v/o ZrO_2 (+ 2 m/o Y_2O_3) was fabricated to full density at temperatures ranging from 1400°C to 1650°C to increase the size of the $\text{ZrO}_2(t)$ grains. Although SEM

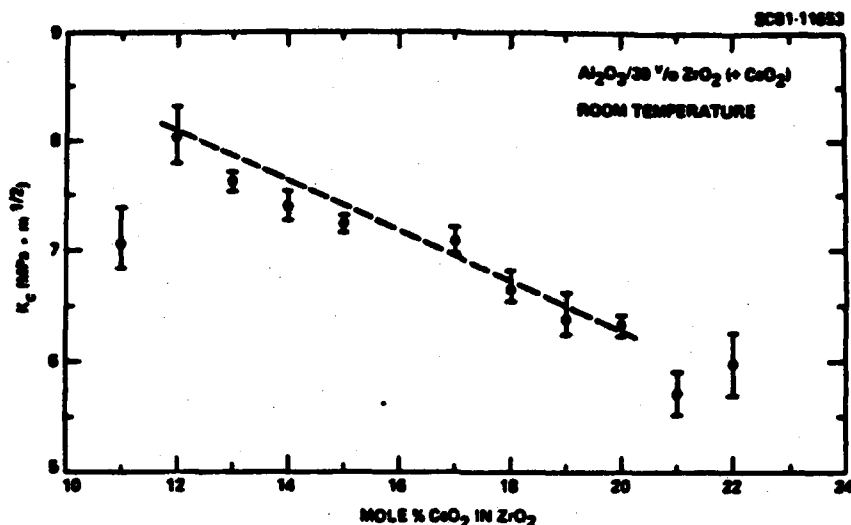


Fig. 8. K_c vs Co_2 content in tetragonal phase field.⁶

micrographs have been taken of etched, polished surfaces to show that the ZrO_2 grain size does increase with increasing fabrication temperature, actual grain size determinations have not been made. XRD examinations show that the ZrO_2 is all tetragonal regardless of fabrication temperature. Figure 9 illustrates K_c vs fabrication temperature (i.e., $D < D_c$). Although these data are preliminary, they do indicate that K_c increases with increasing grain size (D). They also suggest that a maximum grain size (D_{max}) exists for optimum toughness where $D_{\text{max}} < D_c$.

CONCLUDING REMARKS

The end-point thermodynamic approach to retention of tetragonal ZrO_2 and its contribution to toughness appears to be useful in explaining observed phenomena. With regard to phase retention, it not only explains why a critical size exists, but also directs the fabricator to possibilities of increasing the critical size to allow phase retention within the constraints (i.e., grain growth) of current fabrication technology. With regard to toughening, it correctly describes the limitation of the transformation toughening concept, i.e., decreasing toughness with decreasing $|\Delta G_c|$ (viz. increased temperature and alloy content). It can thus be seen that there is a competition between phase retention and toughening; conditions for phase retention are relaxed by decreasing $|\Delta G_c|$, but at the same time, decreasing $|\Delta G_c|$ decreases toughness. It has been this author's experience that a resolution of this dilemma is to increase our fabrication skills in limiting grain growth during densification. A solution to this problem would open up the area of using, e.g., the HfO_2 transformation, which has a much greater

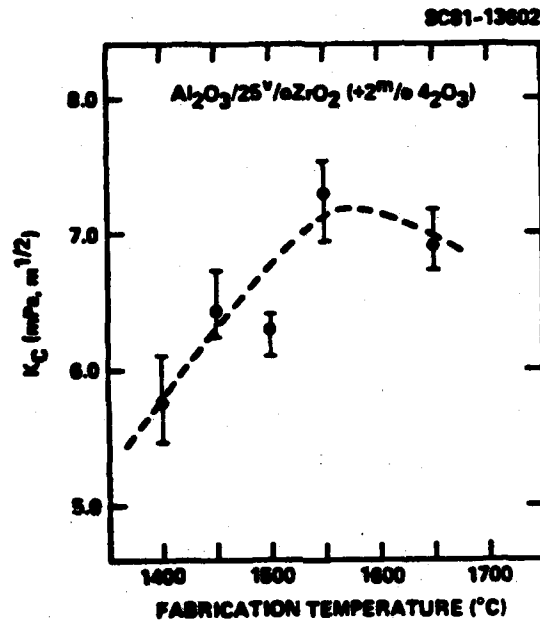


Fig. 9. K_c vs fabrication temperature.

$|\Delta G_c|$ at room temperature than the ZrO_2 transformation and would be a much better toughening agent at higher temperatures than tetragonal ZrO_2 .

It has been amply demonstrated that the transformation toughening concept not only leads to toughening, but also to strengthening, e.g., strengths > 1.2 GPa have been achieved in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite system.⁶ At the same time, however, the reader should remember that K_c is only one factor controlling strength, viz. crack size and distribution also controlling strength and strength scatter, but these two factors are mainly controlled by fabrication.

One final remark is in order. The strengthening derived from tetragonal ZrO_2 (or some other fast transformation) is due to two phenomena: the toughening due to stress-induced transformation at the crack front and surface compressive stresses induced by the molar volume increase associated with a stress-induced transformation at the surface.² Unlike other ceramics, surface machining or particle impact of materials that incorporate tetragonal ZrO_2 produces a strengthening effect. The conditions under which this effect can be optimized are certainly worthy of further scientific exploration.



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